Measuring VOCs in Christchurch ambient air: using SIFT-MS Technique

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by

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Abstract

The project is aimed at monitoring the volatile organic compounds (VOCs) that may be regarded as undesirable in Christchurch's ambient air. Nine VOCs viz NH_3 (ammonia), C_2H_4 (acetylene), C_3H_6 (propene), CH_3OH (methanol), C_2H_5OH (ethanol), CH_3CHO (acetaldehyde), C_6H_6 (benzene), C_7H_8 (toluene) and C_8H_{10} (xylene) were selected to be examined diurnally and seasonally. The samples were taken from various areas around the city. The selected ion flow tube mass spectrometry (SIFT-MS) technique was chosen as the analytical technique for the study as its fast analysis time and high sensitivity (10 ppb to 40 ppm) give it a significant advantage over more conventional methods. Among the results found were unexpected converse behaviour of the dominant species C_3H_6 (propene) and CH_3OH (ethanol). In winter, C_3H_6 (propene) was the dominant pollutant of the nine selected VOCs whereas in summer it was C_2H_5OH (ethanol). Further, the concentration ratios of C_6H_6 (benzene) to C_7H_8 (toluene) are different from the value reported in other cities for urban atmospheric air. The presence of these species at the concentration levels found in the atmospheric conditions prevailing here are sufficiently high to be of concern and a monitoring program is advised.

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Friends, flatmates, family, colleagues, and etc. for their sympathy and help in samplings, creating pleasure environment for doing this work

I thus use this passage to express the feeling in my mind.

There's rare and special quality in the way some people live-

However, busy they may be, they still have time to give,

A thing you ask or need, they'll do their very best,

No matter what the task is or how simple the request,

Kindness just comes naturally to this rare and selfless few,

Special, giving people just like you !

(Unknown author)

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Chapter 1 Introduction

1.1 What will be written in this Chapter

In this chapter the definition of air pollution, sources and effects will be briefly described. Then the air pollution situation in Christchurch will be discussed .

1.2 Air pollution

This problem has been observed and studied for centuries since the Roman Era and has become more seriously discussed with the general recognition that air pollution concentration can affect human health and welfare. Recently, global concerns of air pollution and their relevance to climate change as well as pollution at local levels such as 'smog' in Christchurch city during the winter time have added impetus to the study of air pollution.

1.2.1 Definition

The definition of an air pollutant that is being used in this thesis is Spronken-Smith's definition (2003) which is " substances which, when present in the atmosphere under certain conditions, may become injurious to human, and animal, plant or microbial life, or to property, or which may interfere with the use and enjoyment of life or property."

The major problem of air pollution in Christchurch (ECan, 2003) comes from particulate matter which is "very small liquid and solid particles floating in the air. Of greatest concern to the public health are the particles small enough to be ed into the deepest parts of the lung. These particles are less than 10 microns ameter--about 1/7th the thickness of a human hair--and are known as PM_{10}".

1.2.2 Emission Sources

Air pollution may arise from natural processes and human activities. The natural phenomena such as volcanic eruptions and forest fires rarely occur and mostly have transient adverse effects on humans. Further the environment has the ability to counteract this kind of air pollution coming from natural process. For example, respiratory gas from plants is balanced by the photosythesis mechanism.

Anthropogenic or man-made processes are different from natural processes in that they are derived from human activities. These processes include emissions of volatiles in chemical species from the agricultural, domestic and the industrial sectors. These emissions may be classified as mobile sources as in automobiles and stationary sources for factories.

Two examples of anthropogenic pollutants are methane and carbon dioxide. Methane, one of the greenhouse gases, is generated on the farm or paddy field areas. Carbon dioxide is emitted from combustion processes e.g. incinerators, boilers and the transport sector.

1.2.3 Effect

The presence of air pollution in the atmosphere obviously affects the environment in several ways. The impact of air pollution depends on the concentration of pollution and the duration of pollution. Some consequences of air pollution are;

- Mortality and desease of human, animals and plant
- Climate change: unusual droughts and flooding disasters
- Ozone layer depletion: excessive UV radiation causing skin cancer
- Acid rain that damages both vegetation and buildings
- Creation of an area of local smog, which is a critical problem during winter time in Christchurch
- Reduced visibility, which affects the physiognomy and aesthetics of the city, causing traffic accidents.
- Social impact in the sense of community concerns on health and quality of life

1.3 The Situation in Christchurch

Smog occurs in many cities around the world. Smog buster (2000) reports that there are many places facing this kind of air pollution, arising from different factors. The major reasons are local climate, geography and population. Examples of large cities that have a history of smog-based problems are London, Tokyo, and Los Angeles.

Environment Canterbury, ECan (2003) describes the air pollution problem in Christchurch as mainly caused by geography and climate. During winter, the topography of Christchurch produces temperature inversions that occur over the city and the air pollutants, particularly PM_{10}, are produced throughout the cold night and cannot be dispersed. These situations lead to the occurrence of high pollution nights between May and August. Around 4 pm, people start heating their homes and at this time temperature inversions are most likely to occur. As a result, particulate pollution levels are normally highest between 4 pm and 10 pm.

1.3.1 History of Smog

Smoke is considered to be the major atmospheric pollutant in Christchurch (Van, 2001). Van also describes the timeline of this situation as follows:

" The first known press report of smoke nusiance was recorded in Christchurch on 8th of August 1869 and the main contributor at that time was domestic heating. The Clean Air Act was introduced in 1972. Later the council defined the Clean Air Zone in which only approved heating devices can be installed."

There have been studies of air pollutants from various sites around Christchurch. ECan (1998) has also formulated an emision inventory that elucidates the situation and shows that apart from fuel burning emissions from domestic heating, traffic will also grow to be a considerable source of air pollution in the near future.

1.3.2 Topography

Christchurch city is surrounded by diverse geographical features such as the Pacific Ocean, the Port Hills, and the Canterbury Plains. Morever, the city lies over a flat reclaimed swamp area that leads to high moisture in the air. The low temperature during winter, especially at night, leads to high air pressure and the temperature difference of each air layer forms a warmer blanket that traps the air pollutants. During the cold nights, the temperature inversion occurs with clear sky and no wind. These critical factors combine to create high pollution nights in Christchurch. As Andrew (2002) says "It is obvious that topographically controlled atmospheric processes have a significant influence on air pollution concentrations."

1.3.3 Emission sources

Household fires, vehicle emission and factories have been considered as the three major causes of air pollution in Christchurch city during the cold period. Environment Canterbury (ECan) indicates that 90 per cent of Christchurch's winter particulate matter comes from domestic wood and coal burning. Motor vehicles release 4 per cent with industry producing 6 per cent. (Figure 1.1)

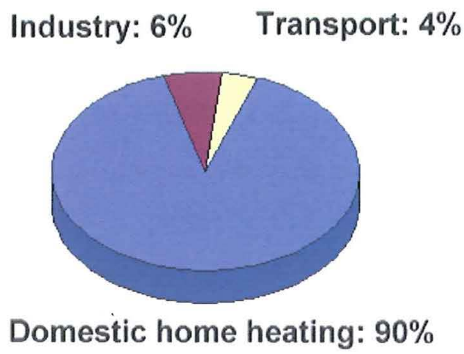


Figure 1.1 Air pollution emission sources by sectors

Among domestic home heating, ECan argues that two-thirds of the particulates associated with domestic home heating are released from open fires and wood burners, while coal burning contributes the remaining third.

Problematic domestic burners often accompany low-income households and rental properties. One reason for the coincidence of domestic burners with low income housing is that electricity prices for heating are unaffordable for these households and there is no incentive or economical way to install any electrical heating appliances when it is not a permanent residence.

1.3.4 Meteorology

According to the location, the meteorological conditions of the city are complex and these relate to the dispersion of air pollutants. A typical situation arises in the following way. The settled anticyclonic system leads to the development of temperature inversion and light winds. The temperature inversion means little vertical mixing of polluted air with a resultant poor dispersion. Air pollution in Christchurch therefore results from the interaction of the local geographic (Sturman, 2002) factors, such as the terrain and local climate, with the distribution of emission sources.

CAPS2000 (2000) determined that the pollution problem in Christchurch resulted from increased domestic emissions in the winter when the city was often subjected to stable nocturnal atmospheric conditions that resulted in poor dispersal through the night. A build –up of the pollutants is the result. Furthermore, complex airflows are the result of local drainage flows from surrounding terrain and the sea/land breeze system. Anticyclonic conditions in winter with clear skies and light winds (development of inversions) and local topographical influences cause the convergence of cold air drainage over the city.

1.3.5 Effect

There have been several papers reporting the effect of air pollution on the health of people in Chrischurch. For example, Wilton (1999) estimated the annual loss of more than 300,000 person days during which people's activities may be restricted. A further consequence is the increasing use of medications for respiratory illness and an estimated 40-60 hastened deaths per annum of people already suffering from cardiopulmonary and respiratory disorders that are exacerbated by pollution levels.

The public have also complained about lack of visibility within the city (The Press, 2002) especially the pedestrians, automobile drivers and cyclists.

1.3.6 Measurement of Pollution

There are many methods to measure air pollution that vary in cost, ease of use and accuracy. The monitoring period is also an important parameter and can vary from long term, short term, continuous, peak to average. Futher, these measurements can be surrogates, real-time, active, passive, etc.

The real time methods give high resolution measurements at a single point. Other concerns are the size of area being sampled, the budget, the security of the equipment, topography, and location of sources. Current monitoring methods employed by ECan at their St.Albans site include a Tapered Element Oscillating microbalance (TEOM).

The TEOM uses a small pump that sucks air through a filter at a constant rate. The weight of the filter changes with the amount of PM_{10} in the air. Increasing PM_{10} on the filter increases the frequency of a small vibrating element in the machine. The TEOM then calculates the amount of PM_{10} particulate material from the changed frequency of vibration. ECan uses this instrument for monitoring PM_{10} at 10 minute intervals to measure the mass of PM_{10} over the sampling period. These data are used to calculate an average number density of PM_{10} between 9 am to 9 am on a daily basis. This data is published on their website.

1) Monitoring

Air quality has been monitored in Christchurch for decades (ECan, 2002). Historically smoke has been monitored in various suburbs of the city and in 1988 a permanent monitoring site was established in the suburb of St.Albans. The pollutants that are measured continuously at this site are suspended particulate (PM_{10}), SOx, NOx, CO and lead (Pb). There are now four air monitoring sites around Christchurch, run by ECan: Hornby, St.Albans, Aranui and Hoon Hay. The two latter sites are mobile stations which are shifted annually.

2) Regulation

There have been several attempts to reduce air pollution in the city, starting from the Health Act in 1956 concerning nuisance control. In 1972, the Clean Air Act was introduced and the regulation under this Act became the major air pollution control legislation in New Zealand. The Resource Management Act (RMA) 1991 section 7 also outlines the framework of air quality management.

At present, the air quality guideline for New Zealand is adopted from the World Health Organization (WHO), and USA. EPA by the Ministry for the Environment (MfE). These guidelines are summarized in Table 1 following:

Table 1.1 New Zealand air quality guideline

Air pollutants	**Averaging period**	**Concentration ($\mu g/m^3$)**
Particulate (PM_{10})	24 hour Annual	120* 40
Sulphur dioxide (SO_2)	10 min 1 hour 24 hour Annual	500 350 125 50
Carbon monoxide(CO)	1 hour 8 hour	30 10
Ozone(O_3)	1 hour	150

	8 hour	100
Nitrogen dioxide(NO_2)	1 hour	300
	8 hour	100

* In March 1996,the Canterbury Regional Council adopted a monitoring and reporting guideline for PM_{10} of 50($\mu g/m^3$)

3) Planning, project & timeframe

ECan, in the chapter on air in the proposed Natural Resources Regional Plan (NRRP) prepared under the Resource Management Act 1991, is seeking to reduce wintertime 'smog' in Christchurch. The solution is based on phasing out solid fuel heating in half the homes in Christchurch (60,000) (Gunsey, 2002).

ECan proposes the following time frame to implement their legislation:

* from 2003- no burners can be installed in new homes or homes that don't have the ability to burn wood or coal.

* from 2004- only burners meeting a new low emission standard of 1 gram of particulate per kilogram of fuel burnt (1 g/kg) and 65% thermal efficiency can be installed (the current Australian New Zealand Standard 4013:1999 is 4 g/kg with no thermal efficiency criteria).

* from 2006- open fires will be banned.

* from 2008- or 15 years after the date of installation, existing wood and coal burners not meeting the low emission standard (above) will be banned .

4) Clean heat project introduction

Gunsey (2002) also mentioned that in order to mitigate the potential impact of people moving to non-solid fuel heating, ECan is to implement a financial incentive and assistance programme to fund changes to non-solid fuel heating and to improve household insulation.

This has prompted the introduction of two campaigns by Christchurch City Council (CCC): Helping Hand for Heating and Warmer Homes. The former resulted in 6,500 homes being converted away from coal and open fire use. The programme was given public submission during June last year (2002) and is scheduled to run for 11 years.

This regional regulatory action is to be backed by an educational campaign, and aided by a 38.5 million dollar financial incentive and assistance programme to convert wood and coal fires to electricity and gas heating and to improve energy efficiency. (Gunsey, 2002)

Alongside the programme, an extensive public education programme is proposed through home shows, local newspapers, household flyers, fact sheets and meetings with key community groups. But in opposition to this trend towards removing wood burners from Christchurch homes, is the recent announcement by Meridian, the largest electricity supplier in the Christchurch area, to increase their prices by up to 30 percent (the Press, 2003).

1.4 What research has been done in relation to this matter?

1.4.1 Research work, models.

There has been considerable previous research work on air pollution in Christchurch such as CAPS2000, Smogbuster 2000, ECan emission inventory and theses by Peyzman and Senaratne.

CAPS2000, Christchurch Air Pollution Study, involves various local, national and international scientists and seeks to further understand meteorological controls on wintertime smog episodes. The observation programme occurred in the winter of 2000, with an intensive period in July.

Gilmour (2000) conducted the Smogbuster CHCH2000 research project to find out the appropriate strategies for elimination and prevention of smog in Christchurch. This collection of papers focuses on alternative ways to cope with air pollution such as renewable energy, energy efficiency and new technology.

ECan has established a monitoring programme of air pollution in Christchurch. As a result several reports such as "Christchurch inventory of air emissions", "Monitoring of Carbon Monoxide on Riccarton Road", "Results of Hazardous Air Pollutant Monitoring in Christchurch", have been published.

Senaratne's (1999) research focuses on ambient level of benzo(a)pyrene(BaP) and BTEX (benzene, toluene, ethylbezene and xylenes) and metals present in Christchurch atmosphere. This study also recommended measurements to be obtained at breathing height to examine the human exposure due to air pollutants. Peyzman (2002) carried out research in modeling the pollution emission plume direction and concentration according to meteorological factors.

1.4.2 Measurement Techniques

There are two general classes of methods commonly employed for monitoring air quality: active and passive. These classes of methods can be viewed in the array shown below.

	Real Time	**Not Real Time**
Active	TEOM,Dusttrack, BAM, ATOFMs, SIFT-MS, etc.	Filter samplers, impactors, SIFT-MS, GC-MS etc.
Passive		Palmes, other diffusion samplers

- *Active sampler methods* collect pollutants from different sites for subsequent analysis in the laboratory. The samples can be stored for a short period of time. The example is a Mini or High Volume instrument which uses gravimetric methods to analyse the samples.
- *Passive Sampling methods* are methods where the samples are collected over a period of time and subsequently analysed in the laboratory. One measurement technique uses a Palmes diffusion tube. This methods provides some measure of temporal resolution.
- *The real –time methods* give high resolution measurements at a single point but at high operational cost e.g. TEOM owned by ECan, and DustTrak owned by Geography Department, University of Canterbury for measuring and recording airbone dust concentration .

1.4.3 Compounds

From a literature survey, it was found that many publications concerning air pollution in Christchurch reported only the major air pollutants that are listed in the National Guideline. The principal pollutants that are monitored under the ECan program are PM_{10}, SO_2, NO_2, CO, and PAH (poly-aromatic hydrocarbons). The Geography Department, University of Canterbury, does research on the effect of PM_{10} concentration on visibility and exposure to NO_2. There are also many other volatile compounds present in the Christchurch atmosphere, but these compounds are not well studied. These compounds include acetaldehyde and toluene derived from combustion processes. Even at low concentration, these species can harm or irritate living organisms.

1.4.4 Data Availibilty

Data on atmospheric conditions relating to air pollution in Christchurch can be obtained from various sources in either hard copy or electronic form. The main agency is ECan. However, the Geography Deparment of Canterbury University and Christchurch International Airport also collect meteorological data such as wind speed and direction, temperature and precipitation.

Data of CAPS2000 were gathered from a network of automatic weather stations, instrumented towers, SODAR (Sound Detecting And Ranging or Acoustic Radar) and several tethered ballooon sites, as well as six air quality sites. The July 2000 records show that there are complex relationships between PM_{10} concentrations and meteorological conditions.

1.5 The objective of this study

The conventional techniques, mentioned above, are very time consuming (typically hours) in achieving their results and are also not sensitive enough to monitor very low concentrations of gaseous volatile compounds, VOCs (volatile organic compounds). This study uses a new technique (SIFT-MS) that detects the volatile air pollutants down to levels of 10 ppb in seconds. The primary objectives of this study are:

1) To examine the amount of pollutants of interest collected from various emission sources and from the ambient city air at different points and times during the day over a year to determine their concentration gradients and to gain a better understanding of the nature and origin of VOC ambient pollution.
2) Establish a library of composition profiles of possible emission sources, such as combustion appliances and motor vehicles.

1.6 Scope of research work

In this study, there were numerous compounds at low concentration in the samples examined. A large number of VOCs could be detected from city air using the SIFT-MS technique but the nine compounds selected for study in this work were chosen for their dominance and potential hazards. These compounds include NH_3 (ammonia), C_2H_4 (ethylene), C_3H_6 (propene), CH_3OH (methanol), C_2H_5OH (ethanol), CH_3CHO (acetaldehyde), C_6H_6 (benzene), C_7H_8 (toluene) and C_8H_{10} (xylene).

1.6.1 Compounds

1) Ammonia

Ammonia (NH_3) is a highly water-soluble, colourless, irritant gas with a unique pungent odour with molecular weight of 17. This compound is extensively used as a component of fertilizer and animal feed. Ammonia is a product of protein catabolism, thus it is found at very high concentration in animal buildings. It was widely used for refrigeration before being replaced by Freon.

Ammonia gas can cause inhalation injury when it reacts with tissue water to form the strongly alkaline solution, ammonium hydroxide.

2) Ethylene

This compound has a molecular formula C_2H_4 and molecular weight at 28. Ethylene is a biogenic volatile organic compound, also known as ethene, mainly produced by plants since it is the plant growth hormone.

3) Methanol

The molecular formular is CH_3OH, and the molecular weight 32.05. Methanol is a polar liquid with a noticeable odour when crude. It is a clear colorless, very mobile flammable liquid, and is miscible with water, alcohol and ethers.

Methanol is synthesised from natural gas, and used in the manufacture of formaldehyde, used as antifreeze for automobiles, and is a common solvent. It is also known as wood alcohol. In New Zealand, major uses of methanol include the manufacture of Methyl Tertiary Butyl Ether (MTBE) which is a petrol additive to increase the octane rating.

If ingested, methanol causes visual impairment, irritates mucous membranes and the upper respiratory tract.

4) Propene

The molecular formula is $CH_3CH{=}CH_2$, and the molecular weight is 42. Propene is also known as methyl ethylene. It is a colorless unsaturated hydrocarbon gas. A small amount of an unpleasant-smelling gas such as a thiol may be added to provide an olfactory warning in the event of a leak. As the second member of the alkene series of hydrocarbons, it is fractionated from natural gas and is a chemical intermediate in the manufacture of organic chemicals, including polypropylene plastics. Propene may be harmful if inhaled. It is an asphyxiant at high concentrations.

5) Acetaldehyde

Molecular formula is C_2H_4O and its molecular weight is 44.06. Acetaldehyde reacts with oxidizers, halogens, amines, strong bases, and acids. It oxidises exothermally in air to acetic acid.

Acetaldehyde is colorless, and has a pungent, suffocating odor. At dilute concentrations it has a fruity and pleasant odour, indicative of a leafy green taste. It is an intermediate product from the respiration of some plants and is a product of incomplete wood combustion in fire places and woodstoves, coffee roasting, tobacco smoke, vehicle exhaust fumes, coal refining and waste processing. Acetaldehyde is formed in the body from the breakdown of ethanol; it is a component in the exhaled breath following the consumption of alcoholic beverage. This compound irritates the eyes, skin, and respiratory tract in humans. At extremely high exposures, respiratory paralysis and death may occur.

6) Ethanol

It has the molecular formula as CH_3CH_2OH with molecular weight 46 and is also known as ethyl alcohol, grain alcohol, and EtOH. Ethanol is a clear, colourless liquid with a characteristic, agreeable odour. In dilute aqueous solution, it has a somewhat sweet flavour, but in more concentrated solutions it has a burning taste. Ethanol is made up of a group of chemical compounds whose molecules contain a hydroxyl group, -OH, bonded to a carbon atom. It is a highly flamable liquid and complete combustion of ethanol results in CO_2. In the USA, it is blended with vehicle fuels from 10 -85 percent. At high concentrations , inhalation causes central nervous system depression and loss of behaviour inhibitions.

7) Benzene

The molecular formula is C_6H_6, and the molecular weight 78.12. When less than pure it is called benzol.

It is a clear colorless – to- light yellow, volatile, flammable liquid with an aromatic odour. It oxidises on heating, is slightly soluble in water and is miscible with alcohol, ether, chloroform, acetone, carbon tetrachloride, carbon disulfide, oils, and glacial acetic acid.

There is sufficient evidence to show that prolonged exposure to this compound can cause leukemia either alone or in combination with other chemicals.

Benzene occurs in tobacco smoke. Since benzene is a constituent of auto exhaust and fuel evaporation, it concentrates mainly in areas of heavy motor vehicle traffic and around gas stations.

8) Toluene

The molecular formula is $C_6H_5CH_3$, and the molecular weight is 92.15. Toluene is a colorless volatile liquid with a sweet pungent odour. It is a produced from incomplete burning of fuels, but is primarily emitted from evaporative sources derived from coal tar or from the catalytic refining of petroleum naphthas.

Toluene is insoluble in water, soluble in alcohol and ether and boils at 111°C. It is used as a chemical intermediate, for explosives, and is a component of high-octane gasolines.

Toluene causes severe irritation and is destructive to tissues of the mucous membranes, upper respiratory tract, eyes and skin. It causes, coughing, headaches, nausea, vomiting, and lung irritation.

9) Xylene

The molecular formula is C_8H_{10} and the molecular weight is 106.18. Xylene is known as1,2-dimethyl, dimethylbenzene, and o-xylol. It is also a component in the maufacturing process for high performance polymer, plasticizers, insecticides, and motor fuels and used as a solvent in the printing, rubber, and leather industries. Xylene is a clear and colorless liquid with a sweet, aromatic odor. It is a very dangerous fire hazard when exposed to heat or flame. The combustion of xylene may produce irritants and toxic gases to the central nervous system. Long term exposure results in pulmonary damage.

People who breathe high levels of xylene may experience dizziness, confusion, and a change in their sense of balance. This chemical can be broken down in sunlight and become less harmful. It can be smelled in the air at 80 ppb.

1.6.2 Using SIFT-MS as a new technique for measuring air pollutants/trace gases in ambient air, exhalation and point sources.

This research requires the analysis of contaminated Christchurch air for impurities at trace levels. A suitable accurate analytical method is needed for this work to detect and quantitatively measure gases at low concentrations. There have been several research studies using the Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) technique, developed by the Chemistry Department of Canterbury University, for detecting trace gases in ambient air (Gunn, 2001) exhalation (Senthilmohan et al, 2000), (Wilson et al, 2001) and emission point sources (McKelvie, 2002).

In the next chapter the experimental method will be explained. The research began from preliminary tests in the laboratory with SIFT-MS, confirming the use of Mylar bags for collection and sample storage. The selection of preferred sites in the city were made in conjunction with the existing sites used by ECan and the Geography Department, University of Canterbury.

Chapter 2 Experimental Method

2.1 Introduction to SIFT-MS methodology

Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) is a very sensitive and rapid technique for analysing trace amounts of volatile chemical species in air. When dealing with very low concentrations or small amounts of compounds in the parts per billion range or less, it is important to have a sampling methodology that preserves the integrity of the sample. In mixtures where there are many analytes, there may be several contenders for a particular mass peak. In these cases it is necessary to utilize the known ion chemistry of the different ion precursors (H_3O^+, O_2^+, NO^+), to identify the analyte. Different precursor ion species can be selected, by switching the upstream mass filter of the SIFT-MS.

To be effective as chemical ionization agents, the selected ion precursors must not react at a significant rate with the major components of air e.g. N_2, O_2, CO_2, H_2O and Ar but must react effectively with the compound of interest in the sample. The precursors, H_3O^+, O_2^+, and NO^+ have these characteristics and are widely used with both organic and inorganic compounds. H_3O^+ is suitable for analytes with medium to high proton affinity while NO^+ reacts rapidly with low ionisation potential species. O_2 has a much higher ionization potential than NO and thus O_2^+ is more reactive than NO^+ and reacts well with species that are not suitable for H_3O^+ nor NO^+.

2.1.1 The principle

The analytes of interest are ionised by the mass-selected precursor ions such as H_3O^+, O_2^+, and NO^+ .These precursor ions are generated in the ion source, using a helium/air mixture in a microwave discharge. After ionisation and mass selection, the precursor ions are injected into the flow tube where they are carried along the tube in a flow of helium down to a sampling port at the down stream end. A schematic diagram of the SIFT-MS instrument is shown in Figure 2.1.

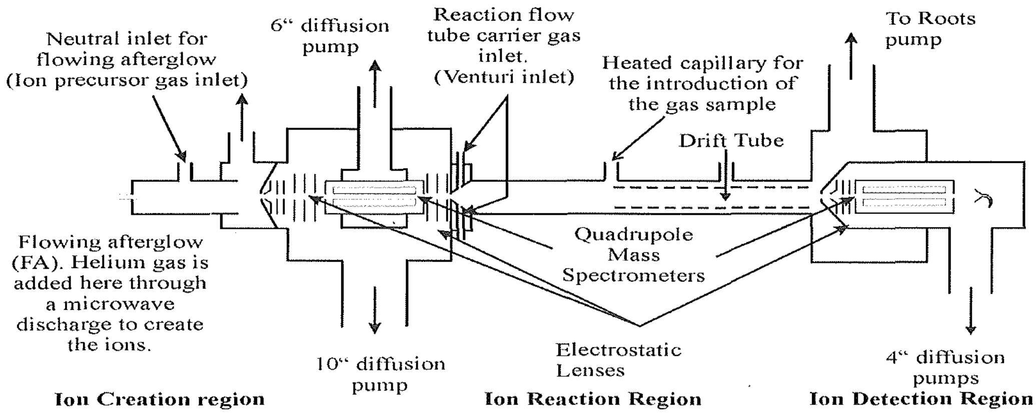


Figure 2.1 Diagram of the Selected Ion Flow Tube Mass Spectrometry (SIFT-MS)

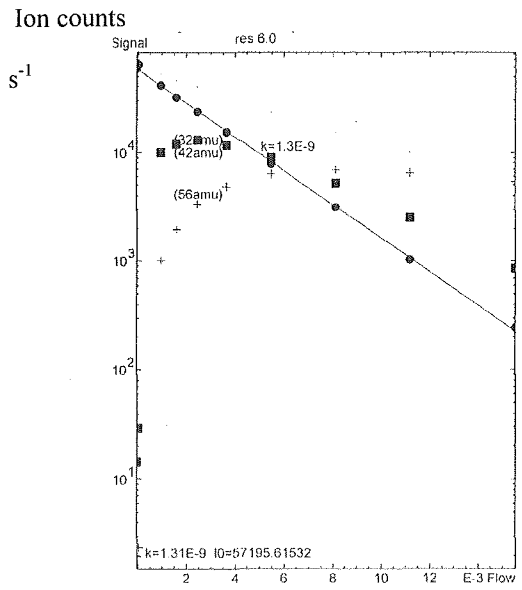
2.1.2 Advantage

The SIFT-MS machine does not require calibration, as the ratio of reactant precursor ion to analyte product ion provides an absolute measure of the analyte concentration in the mixture, providing the rate coefficient (k) for the reaction of the precursor ion with the analyte is known. For example, if we use O_2^+ as the precursor ion for analysing propene (C_3H_6) in the sample, it is necessary to first measure the rate of removal of O_2^+ with the propene and to also examine and measure the branching ratio to all products.

$$O_2^+ \quad + \quad C_3H_6 \xrightarrow{100\%} C_3H_6^+ \quad + \quad O_2$$

$$k = 1.31 \times 10^{-9}\ cm^3/s$$

The rate coefficient is obtained under pseudo first order kinetics from the slope of the semi logarithmic decay of O_2^+ with the propene flow (Figure 2.2). The branching ratios are found by extrapolating the product ratios to zero pressure.



Flow of Propene in Torr Ls-1

Figure 2.2 A semi logarithmic plot of ln [Ion Count] versus neutral flow rate for the reaction of precursor (O_2^+) and propene (C_3H_6). The linear decay of the O_2^+ ion counts (•) and C_3H_6 (▪) and commensurate rise of the secondary product ion counts $C_4H_8^+$(+).

Once, these measured parameters are known for the analyte (e.g. propene) they are programmed into the SIFT database. The sample to be analysed is then added through the heated capillary (100-140 °C) inlet where the reaction of O_2^+ with the VOC (volatile organic compound) occurs. Because the flow of sample gas through the capillary is known, then the number of counts per second at each of the product ions from reaction gives a direct measure of their concentration in the sample. Thus from a single mass scan, the concentrations of all compounds of interest in the sample can be automatically calculated and displayed (see Figure 2.3 as a typical sample mass spectrum).

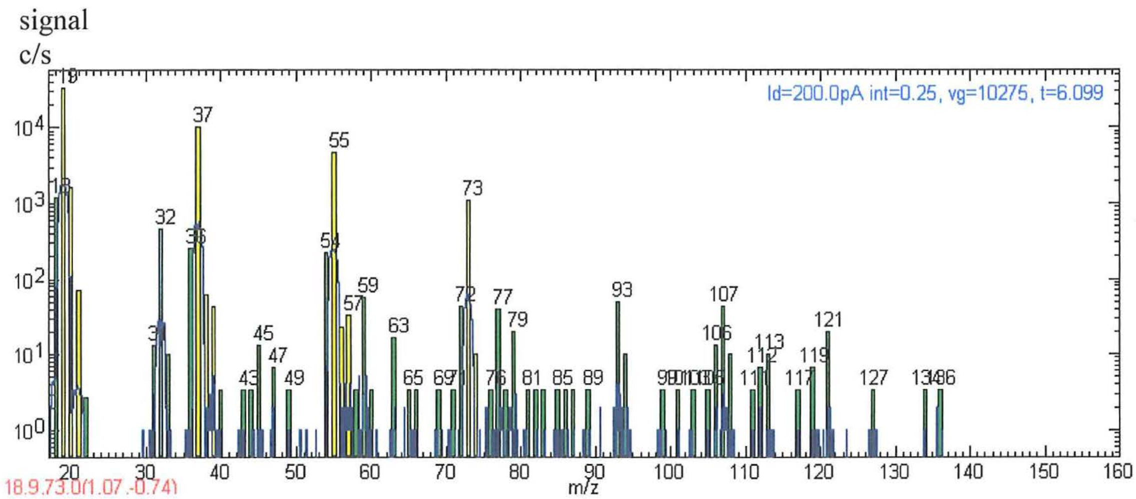


Figure 2.3 Example of analytical result from SIFT-MS

2.1.3 Preliminary test for SIFT

In this experiment, pure propene (C_3H_6) was examined by injecting into the SIFT-MS instrument to obtain the rate coefficient (k) of its reaction with the mass selected precursor (O_2^+). To avoid interference from room air, the sample was sealed in a closed container. Using the 'SIFT for windows' software calculation, k for the reaction between O_2^+ and C_3H_6 was 1.31 x10^{-9} cm^3/s. The main product of the reaction between O_2^+ and C_3H_6 was $C_3H_6^+$. $C_4H_8^+$ was a secondary product arising from the subsequent reaction of $C_3H_6^+ + C_3H_6$.

<u>1) Materials and Equipment</u>

1.1. <u>Chemical</u>

- Propene, (C_3H_6) analytical grade, available from commercial sources.
- Helium gas

1.2. <u>Laboratory equipment.</u>

- The Selected Ion Flow Tube Mass Spectrometer (SIFT-MS) in the Chemistry Department, see Figure 2.4

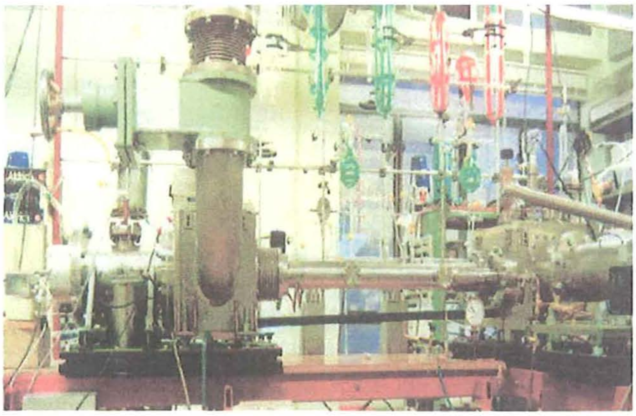


Figure 2.4 Selected Ion Flow Tube Mass Spectrometer (SIFT-MS) apparatus

2) Procedure for investigating reaction kinetics

2.1 The length of flow tube is 50.4 cm.

2.2 The SIFT-MS needs to be warmed up for 2 – 3 hours to heat up the oil diffusion pumps.

2.3 The prepared propene is (purified by a freeze-pump thaw cycle) taken from the Chemistry Department Laboratory and introduced into the flow line.

2.4 Following the generation of the precursor O_2^+ as indicated on the PC monitor, the C_3H_6 is released into the reaction tube and the reaction between O_2^+ and C_3H_6 is monitored.

2.5 The flow rate of C_3H_6 was changed to obtain the rate coefficient (k) of the reaction as discussed in section 3.

3) Results and discussion

3.1 Calculation of Result

From the basic chemical reaction equation

$$A^+ \quad + \quad B \quad \rightarrow \quad \text{products},$$

the rate of reaction between A and B is given by

$$k = \ln \frac{[A^+]_0}{[A^+]} * f([B]) \qquad (1)$$

where $[A^+]_0$ = ion count of A^+ in the absence of B, and f ([B]) = flow rate of B.

Under ion molecule reaction conditions, $[A^+] << [B]$.

For example, in the experiment between O_2^+ reacting with propene, the concentration of O_2^+ (precursor) is known from the ion count and the absolute [B] (from flow rate of neutral, C_3H_6) is known. These quantities are used for calculating the k value, by the "SIFT for windows" software. The slope of the line in the semi logarithmic graph of ion counts versus propene gave a value for $k = 1.31 \times 10^{-9}$ cm^3/s (see Figure 2.2).
When a sample contains an unknown concentration of C_3H_6 in a gas mixture, the amount of C_3H_6 can be calculated from the ratio of the O_2^+ to $C_3H_6^+$ signal.

$$\text{ppb } C_3H_6 = \frac{\text{flow of } C_3H_6}{\textbf{total flow of the sample}} \qquad (2)$$

where flow of C_3H_6 in molecule cm^{-3}s^{-1} $= \frac{1}{t} \frac{I_{\text{product ion}}}{I_{\text{precursor ion}} . k}$ for a single product ion (3)

In equation (3), t is time for reaction in seconds, $I_{\text{product ion}}$ and $I_{\text{precursor}}$ are the relative intensities of the product ions and precursor ions, respectively.

This spectrum shows the $C_3H_6^+$ as the first product (98%) and $C_4H_8^+$ as a secondary product (2%). Thus we can use this result to examine the unknown concentration of C_3H_6 in the further experiments.

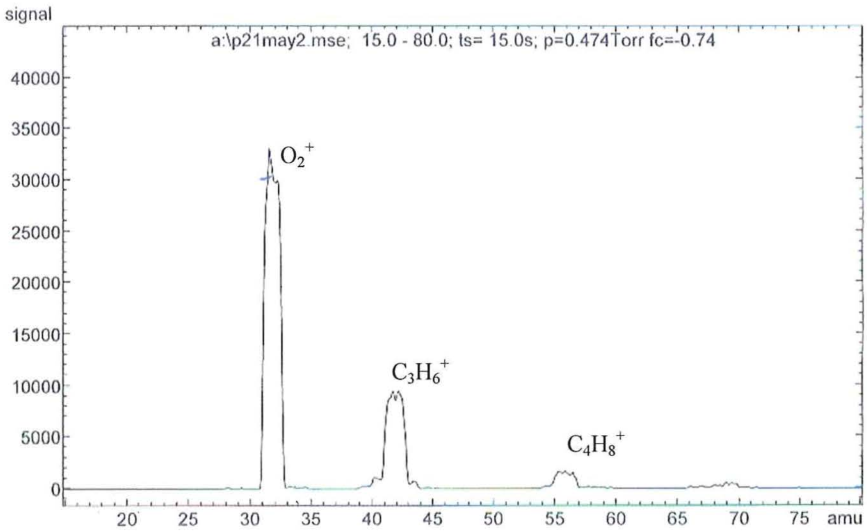


Figure 2.5 Mass spectrum from SIFT-MS obtained by reacting O_2^+ and C_3H_6

The SIFT-MS is a high sensitivity instrument; the compounds of interest can be detected and quantified from 10 ppb to 40 ppm in some cases up to 100 ppm depending on conditions. In all cases the compounds must be volatile.

Since this method has such high sensitivity and can detect trace amounts of volatiles in ambient air, it is possible to have interferences from room air, so the sample is injected from a closed container to prevent this happening.

2.2 Mylar Bag Sampling

In this research the "Mylar foil balloon type" that is often sold at supermarkets for birthdays and other occasions was used for collecting and containing the air samples (Figure 2.6). The bags were used only once.The membrane has minimal oxygen content, is heat (insulating) resistant, impervious to moisture, is strong enough to hold a partial vacuum, and is non-transparent to light. In addition, no technically skilled personnel are required at the sampling site since the samples are easy to handle and no field calibration is needed.

Figure 2.6 Mylar bags used for air sampling

2.2.1 Research work

Air sampling is critical since we cannot see the actual sample so researchers try to be precise using the most reliable sample containers. In grab sampling, widely used for identification of the significant pollutants, a sample of air is collected in a short time. Samples can be collected in evacuated bottles, gas syringes, and bags made of synthetic materials [Godish, 1997].

2.2.2 Cost

There are several types of synthetic material bags available for air sampling e.g. Teflon, Mylar, and Tedlar. Practically, the Mylar bag is least expensive and it provides a suitable quality for research purposes, in that for most of the compounds of interest in this study, it is chemically inert. These balloons are also self sealing and no heat or other chemicals are applied after sampling. Moreover, they are easy to transport from the sampling sites to the laboratory.

2.2.3 Stability Test for compounds of interest

Mylar bags are light, and air and water proof. Test trials were carried out to confirm these properties. Figure 2.7 shows that there is a little difference between concentrations of a test sample of analyte compounds immediately after preparation, after 24 hours and 96 hours containment. The data show that the balloon medium is not reacting significantly with or adsorbing the measured compounds. However, the results from the samples after 96 hours indicate some variation in concentration. These tests confirm the integrity of the balloon for collecting samples provided that analysis is carried out within 24 hours.

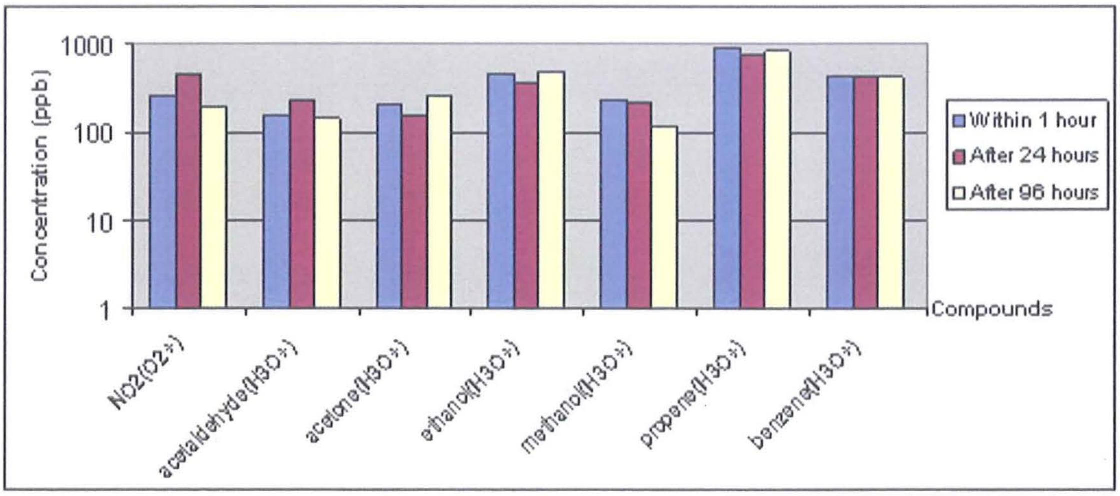


Figure 2.7 the persistence of selected compounds in Mylar bags after different residence times

2.3 Sampling method

2.3.1 Site selection

In order to have a truly representative sampling of pollution concentrations in Christchurch, a natural background concentration must be taken that is representative of the residential, industrial and traffic-congested areas. It is essential that the data collected are characteristic of the location, be it residential or otherwise, and that it does not show undue influence of the immediate surroundings. For example, when the nearby factories start or stop running their boilers, and industries/residences adjacent to the sampling site switch on their space heaters.

All samples were collected at the same height, about 1.5 to 2 meters above ground level. This is considered as the breathing zone since this study focuses on the health impact from air pollutants which people normally encounter by inhalation. The reproducibility of the method was checked by taking several balloon samples of the same air and confirming that there was no significant difference in composition.

Constraints to the ambient airflow were avoided by placing the air intake at least 1.5 metres from building or other obstructions and also away from microscale or local time varying sources. The reason for this is that sampled air should be a well mixed sample so it properly represents the ambient in the region. As a result, any sampling errors are minimized.

For this research, two sampling phases were conducted, one in winter and another in summer to examine the seasonal variation of pollutants. Three sites were selected for the winter sampling and another nine for the summer sampling (Figure 2.8).

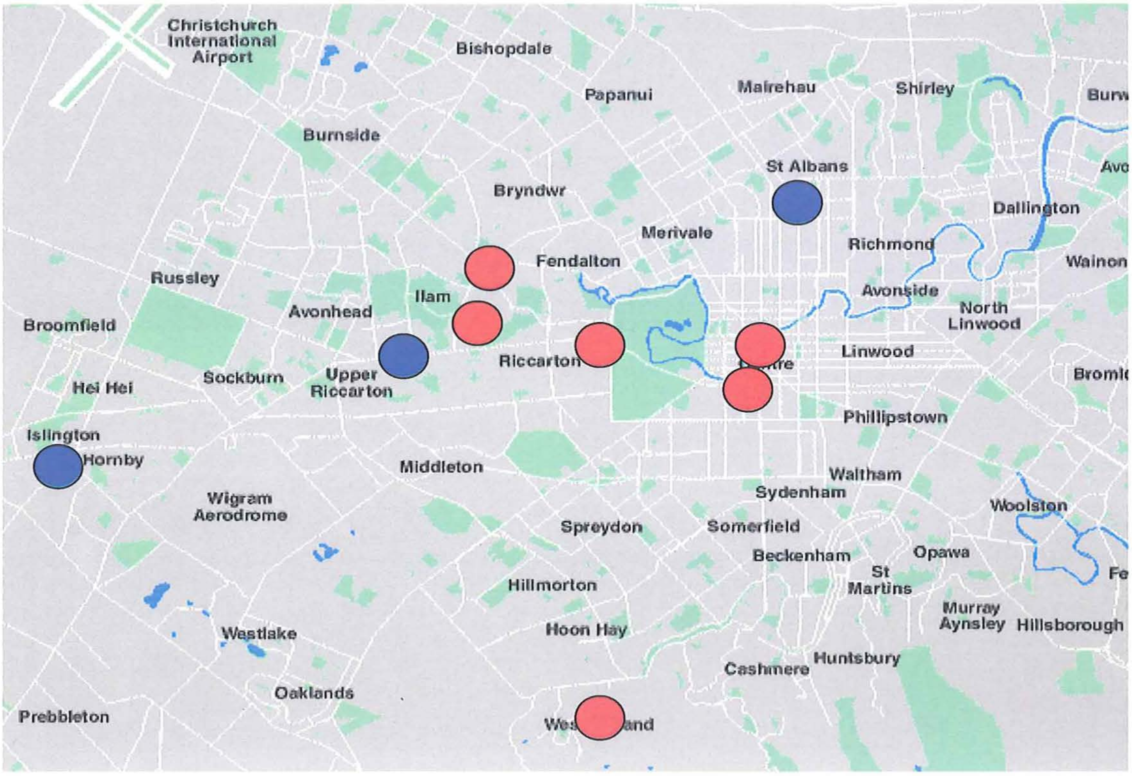


Figure 2.8 Sampling sites around Christchurch city; blue points represent winter sites.

Table 2.1 List of the sampling sites and their representations

Sampling Sites	REPRESENTATION	LOCATION
A. Winter Phase		
South Hornby School	Industrial area	
Bush Inn Mall	Traffic-congested area	Riccarton Road
St. Albans Coles Place	Residential area	
B. Summer Phase		
South Hornby School	Industrial area	
Bush Inn Mall	Traffic-congested area	Riccarton Road
St. Albans Coles Place	Residential area	
corner of Dean Road & Riccarton Road	Traffic-congested area	
corner of Clyde Road & Memorial Avenue	Traffic-congested area	
corner of Colombo street & Moorhouse Avenue	Traffic-congested area	
Worsleys Road.	Background ambient air	
corner of Ilam Road & Riccarton Road	Traffic-congested area	
Bus exchange	Traffic-congested area	Corner of Colombo Street and Lichfield Street

2.3.2 Period

Under normal circumstances the air temperature falls with increasing altitude, but during an inversion the temperature rises instead. During inversions, the wind speed is generally low, thus both horizontal and vertical mixing of pollutants is weakened and so they accumulate in the vicinity of the emission sources.

Samples were obtained during 8.30-11.00 am and 8.30-11.00 pm. During these periods of the day the concentration of pollution is higher, which is the ideal setting to measure for high pollution levels.

2.3.3 Equipment

Major tools for air sampling are basically as follows;

1) Air pump

The air pump is a 250 psi air compressor with high volume inflator Model no.SC827, using 12Volt DC rechargeable battery power source. This compressor was used to inflate Mylar bags on site. All components within the sampling system are inert plastic to avoid contamination. [Gunn, 2001]

2) Mylar bags

Mylar bags are commonly sold at supermarkets for birthdays and other occasions. The industrial name for the Mylar foil balloon material is metallized polyester.

3) Pocket Weather Tracker

A Kastrel Pocket Weather Tracker (Figure 2.9) was used to track wind speed, temperature and humidity. Data was logged three times at the breathing zone (1.5-2.0 metre height) when taking samples at those sites.

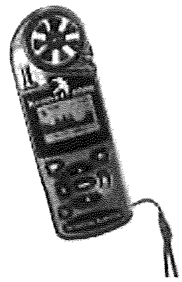


Figure 2.9 Kastrel 4000 Weather Tracker

2.3.4 Procedure

1) Sampling trips were done by days (8.30-11.00) and nights (20.30-23.00) at the selected sites. The dates were randomly chosen from weekdays and weekends during winter and summer.
2) Local temperature, relative humidity and wind speed were recorded by using the Pocket Weather Tracker for each site.
3) At the sites, ambient air was pumped into a Mylar bag by using the assembled equipment as shown in Figure 2.10. After connecting the pump, battery and the vacuum tube together, the pump was started to allow sufficient time for totally flushing the sample train before inflating the Mylar bags. After 5 minutes, the Mylar bags were disconnected and sealed using their self sealing valve.
4) Breath samples were also obtained at each site. The bag was blown up by one subject who exhaled air into a Mylar bag following an acclimatising routine. The

person was required to flush their lungs by deeply inhaling air from the site a few times before blowing into the bag.

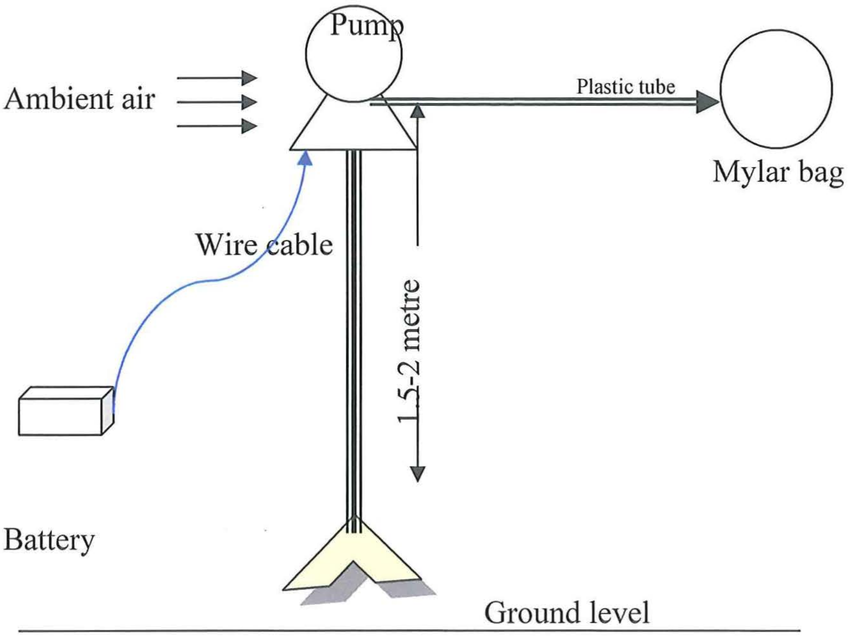


Figure 2.10 Diagram of equipment assemble at site during air sampling

5) The samples from the day trip were analysed by 14:30 the same day. The night trip samples were analysed by 14:00 hours of the following day.

2.4 Meteorological data

To get the overall weather conditions for the sampling sites, the average of certain parameters were obtained from the nearby weather stations. These meteorological parameters are wind speed, wind direction, relative humidity and ambient air temperature for the period when the samples were collected. There are weather stations owned and operated by Environment Canterbury at the Hornby site and the St. Alban site. There is no station at the Riccarton sampling site so the weather data for this site was taken from the station owned by the Geography Department, University of

Canterbury. When no data were available from this site, the site of Christchurch International Airport that is about 5 km west of the sampling site was chosen.

2.4.1 Input from Environment Canterbury

During the 2002 winter, only wind speed and wind direction data was obtained from the Hornby station. Meanwhile, the St. Albans station collected all of the correlated parameters such as wind speed, wind direction, relative humidity and ambient air temperature.

Over the summer period, external temperature data at Hornby was available only for the last date due to the temperature probe being installed on December 17, 2002. (Appendix A). All weather station data were collected at a 3 meter height above ground level.

2.4.2 Input from Geography Department, University of Canterbury

During the winter of 2002, there was a major problem with the logging system and all the data from mid-June until the start of September was lost. As a default position at the Geography Department site, the hourly data from the Christchurch International Airport station were used instead.

For the summer data, CHCH Aero at Geography does not have ten minute data so data were collected from Christchurch, Kyle St, (Lat -43.531 Long 172.607) which is the only Christchurch station with 10 minute data. Appendix B shows the raw data.

2.4.3 On site data recorded; Kastrel 4000

The data described in 2.4.1 and 2.4.2 were collected at different heights of sampling above ground level and not from every selected site. In addition, only wind data is available from the Hornby site while Geography Department and Christchurch International Airport are distant from the sites. Meteorological data was also collected from each site by a weather pocket tracker appliance to support the data analysis (Appendix C).

2.4.4 Publications

Sampling dates were generally selected according to the pollution forecast from ECan. This came by daily e-mail giving a prediction of the likely level of pollution for the evening and night based on the weather condition and forecast. The main pollutant of concern to ECan was the PM_{10}.

This e-mail system is a kind of warning message to the public through media and relevant agencies. An example of the e-mail message is given in Appendix D.

In addition, the related information from the press and television news was also taken into account when selecting nights in which to take samples (The Press, 2002).

Chapter 3 Air Sampling and SIFT Analysis

Precursor ions are formed in a flowing afterglow. An afterglow is a mixture of ions, neutrals, electrons and excited metastable species.Helium gas (BOC instrument grade) is irradiated by a microwave source producing excited helium metastable species in the flow tube. A small flow of moist air (produced by bubbling a small air leak through a water filled saturator) is bled into the Helium afterglow. The helium metastable species ionise the components of the air (N_2, O_2, and H_2O) leading to a series of ion- molecule reactions which produce a mixture of the desired precursor ions H_3O^+, O_2^+ and NO^+. A small fraction of these ions from the afterglow is injected into the upstream quadrupole mass filter. The mass filter is used to select between the precursor ions. An ion selected by the mass filter is focused by electrostatic lenses to the region of a venturi orifice which inject the ion along with a fast flowing stream of helium into the reaction tube.

3.1 Characteristics of each precursor ions

3.1.1 O_2^+

This precursor ion reacts mainly via charge transfer and dissociative charge transfer with small hydrocarbon (HCs) with the exception of methane (CH_4). With methane, O_2^+ reacts very slowly (see Table 3.1) but it does react efficiently with the inorganic compounds NH_3, NO, and NO_2. An example is the charge transfer reaction with propene (C_3H_6).

$$O_2^+ + C_3H_6 \rightarrow C_3H_6^+ + O_2 \qquad \text{........(1)}$$

$k=1.31 \times 10^{-9}\ cm^3/s$

Table 3.1 Reaction of O_2^+ with the given hydrocarbon

CH_4 (methane)	12.61	$CH_3O_2^+$ +H	0.005 (1.2)
C_2H_6 (ethane)	11.52	$C_2H_6^+$ +O_2^+ C_2H_5 +O_2 +H $C_2H_4^+$ +O_2 +H_2	1.1 (1.3)
C_2H_4 (ethylene)	10.51	$C_2H_4^+$ +O_2	1.0 (1.2)
C_3H_6 (propene)	9.73	$C_3H_6^+$ + O_2	1.3 (1.4)
n-C_4H_{10} (*n*-butane)	10.57	$C_4H_{10}^+$ +O_2 $C_4H_9^+$+O_2 +H $C_3H_7^+$ +O_2 +CH_3 $C_3H_6^+$ +O_2 +CH_4	1.4 (1.5)
NO_2 (nitrogen dioxide)	9.79	NO_2^+ +O_2	0.55 (1.0)
NH_3 (ammonia)	10.2	NH_3^+ +O_2	2.6 (2.4)
C_2H_4O (acetaldehyde)	10.2	$C_2H_4O^+$ +O_2	2.3 (3.1)
C_3H_6O (acetone)	9.69	$C_3H_6O^+$ +O_2	2.7(3.3)
C_2H_5OH (ethanol)	10.49	$C_2H_4O^+$ +O_2 +H	2.3 (2.3)
CH_3OH (methanol)	10.84	CH_2O^+ +O_2 +H	2.3 (2.3)
C_5H_8 (Isoprene)	8.84	$C_5H_8^+$ +O_2	1.7 (1.5)

* The measured rate coefficients are listed in units of 10^{-9} cm^3/s. The calculated collision rates (in units of 10^{-9} cm^3/s) are shown in parenthesis.

3.1.2 H_3O^+

The ion H_3O^+ reacts mainly by a proton transfer reaction. If the proton affinities of the hydrocarbons (HCs) are greater than the proton affinity of H_2O (PA H_2O = 691 $kJmol^{-1}$), then proton transfer will occur from H_3O^+ to the hydrocarbon.

- $H_3O^+ + HC \rightarrow (HC{+}1H)^+ + H_2O$ ....(2)

Nevertheless, H_3O^+ does not react with ethane (C_2H_6), methane (CH_4) and propane (C_3H_8) in keeping with their lower proton affinities (PAs) as shown in table below.

Table 3.2 Reaction of H_3O^+ with the given hydrocarbon

Neutral	**PA (kJ mol^{-1})**	**Products**	**Observed Rate***
CH_4 (methane)	543.5	No reaction	<0.001(1.3)
C_2H_6 (ethane)	596.3	No reaction	<0.001 (1.5)
C_2H_4(methane)	680.5	$C_2H_4^+.H_3O$ $C_2H_5^+ + H_2O$	0.063 (1.4)
C_2H_2(acetylene)	641.4	$C_2H_2.H_3O^+$	0.011.(1.3)
C_3H_8 (propane)	625.7	No reaction	<0.001 (1.6)
C_3H_6(propene)	751.6	$C_3H_7^+ + H_2O$	1. 5(1.7)
C_3H_6O (acetone)	812	$C_3H_7O^+ + H_2O$	3.9(3.9)
C_2H_4O (acetaldehyde)	786.5	$C_2H_4O^+ + H_2O$	3.7 (3.7)
C_2H_5OH (ethanol)	776.4	$C_2H_6OH^+.H_2O$ $C_2H_6OH^+ + H_2O$	2.7 (2.7)
CH_3OH (methanol)	754.3	$CH_4OH^+ + H_2O$	2.7 (2.7)
C_6H_6 (benzene)	750.4	$C_6H_7^+ + H_2O$	1.9 (1.9)
C_7H_8 (toluene)	784.0	$C_7H_9^+ + H_2O$	2.2 (2.2)
o-C_8H_{10} (xylene)	796.0	*o*-$C_8H_{11}^+ + H_2O$	2.2 (2.4)
m-C_8H_{10} (xylene)		*m*-$C_8H_{11}^+ + H_2O$	2.3 (2.4)
p-C_8H_{10} (xylene)	794.4	*p*-$C_8H_{11}^+ + H_2O$	2.2 (2.2)

* The measured rate coefficients are listed in units of 10^{-9} cm^3/s. The calculated collision rates (in units of 10^{-9} cm^3/s) are shown in parenthesis.

Rapid proton transfer from H_3O^+ is the common result of reactions for most of the volatile organic compounds (VOCs). In moist air sampling, a fraction of the product ions can 'cluster' with the abundant water molecules to form the monohydrate

($H_3O^+.H_2O$ at m/z=37) and higher hydrated ions. Figure 3.1 shows the result from breath sampling, the yellow bars indicate a peak with water clusters.

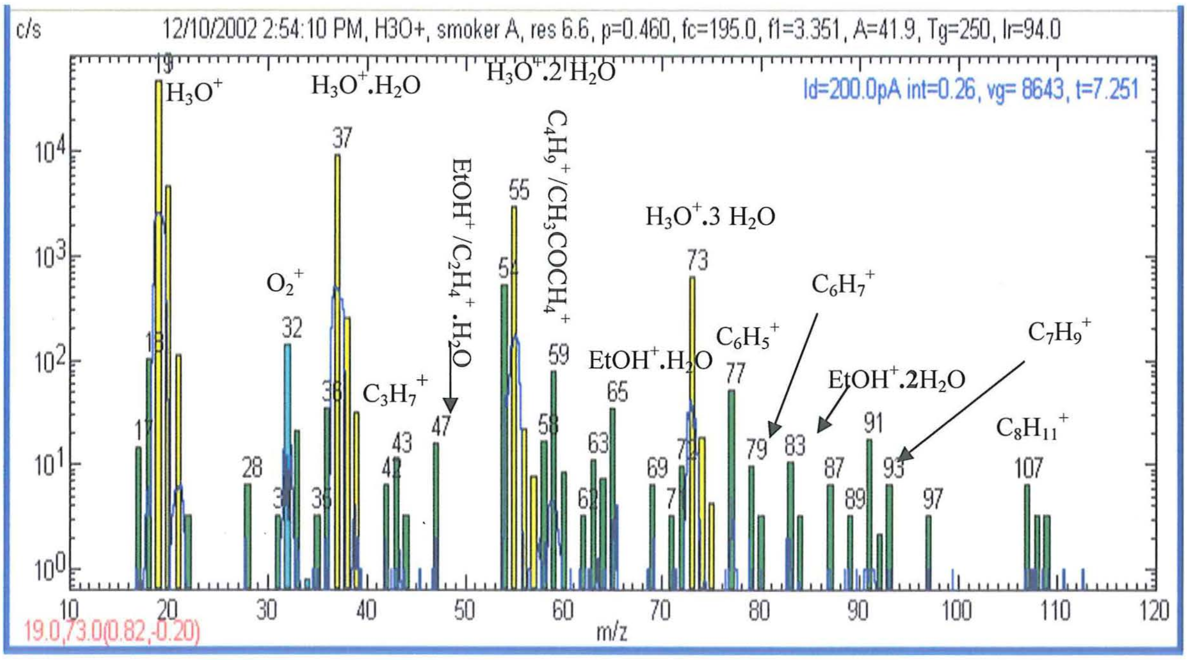


Figure 3.1 Water cluster peaks in breath sampling

3.1.3 NO$^+$

The NO$^+$ precursor ion rapidly reacts with species having a low ionisation potential and provides complementary information to that provided by the previous precursors ions. NO$^+$ reacts with organic molecules by one of three mechanisms when charge transfer is exothermic. Generally, when the ionisation potential (IP) of organic compounds < 9.26 eV, charge transfer will occur and is usually rapid. In addition, hydride ion transfer can also occur producing [M-H$^+$] ions (as for many alcohols and aldehydes) and association producing NO$^+$.M (as for many ketones) [Wilson et al, 2003].

- $NO^+ + c\text{-}C_3H_6 \rightarrow C_3H_6^+ + NO$ ....(3)

$$k = 6.3 \times 10^{-11}\ cm^3\ s^{-1}$$

$$\Delta H° = 11.9\ kJ\ mol^{-1}$$

Table 3.3 Reaction of NO^+ (IP= 9.264 eV) with the given hydrocarbon

Neutral	**IP (eV)**	**Products**	**Observed Rate***
CH_4 (methane)	12.61	No reaction	<0.001 (1.2)
C_2H_6 (ethane)	11.52	No reaction	<0.001 (1.3)
C_2H_4 (ethylene)	10.51	$C_2H_4.NO^+$	<0.001 (1.3)
C_3H_6 (propene)	9.73	$C_3H_6.NO^+$	0.063 (1.5)
c-C_3H_6 (cyclopropane)	9.86	$C_3H_6^+$ + NO	0.45 (1.3)
n-C_4H_{10} (*n*-butane)	10.57	$C_4H_9^+$ +HNO	~ 0.002 (1.5)

* The measured rate coefficients are listed in units of 10^{-9} cm^3/s. The calculated collision rates (in units of 10^{-9} cm^3/s) are shown in parenthesis.

3.1.4 HCO^+

This ion invariably reacts by proton transfer. We use this ion as a precursor to get SO_2 concentrations. SO_2 is a difficult analyte to detect using SIFT-MS methodology because no rapid reaction occurs between any of the traditional H_3O^+, $O_2{}^+$ and NO^+ ion precursors and SO_2. To get round this problem we used the precursor HCO^+ ion, generated from oxirane or ethylene oxide (CH_2OCH_2) which underwent rapid proton transfer with SO_2. A complicating factor is that unfortunately HCO^+ also reacts with H_2O that is always present.

Table 3.4 Reaction of HCO^+ (PA= 636 kJ mol^{-1}) with the given hydrocarbon

Neutral	**PA (kJ mol^{-1})**	**Products**	**Observed Rate***
CH_4 (methane)	543.5	No reaction	0.001 (1.28)
C_2H_2 (acetylene)	641.4	$C_2H_3^+$+ CO	1.36 (1.2)
C_2H_6 (ethane)	596.3	$C_2H_7^+$ + CO	0.12 (1.3)
NH_3 (ammonia)	853.6	NH_4^+ +CO	2.25 (2.4)
c-C_6H_6 (benzene)	750.4	c-C_6H_7 +CO	1.6 (1.6)

Neutral	**PA (kJ mol^{-1})**	**Products**	**Observed Rate***
c-C_3H_6 (cyclopropane)	751.6	$C_3H_5^+$ + CO+ H_2 $C_3H_7^+$ + CO	1.3 (1.5)
H_2O	691	H_3O^+ +CO	2.6 (2.7)
O_2	421	No reaction	$\leq$0.002 (0.25)
HCN	713	$HCNH^+$+CO	3.5 (3.7)

* The measured rate coefficients are listed in units of 10^{-9} cm^3/s. The calculated collision rates (in units of 10^{-9} cm^3/s) are shown in parenthesis.

3.2 Use of precursors

As noted before, the SIFT has two operational modes; a mass- scan mode and selected multiion mode. In the mass scan mode, the instrument examines all VOCs in the sample as in Figure 3.1. The VOCs are identified in the scan according to their mass. The concentrations of each VOC are calculated using the kinetics database from previous SIFT studies of the rate coefficients and product ions of the VOCs. In the multiion mode of operation, the instrument samples only those VOCs of interest (Wilson et al, 2003).

3.2.1 Mass identification

The table 3.4 shows the possible product ions from H_3O^+ reacting with the VOCs listed. The reaction chemistry between the H_3O^+ and the VOCs is summarised in section 3.1.2. For instance, the 43 mass peak that is observed in the SIFT spectrum of HCs in air corresponds to mass 42 which is identified as C_3H_6 or propene. It is also noted that water cluster peaks appear at m/z = 19, 37, 55, and 73. Water clusters of other product ions are also found in the reactions with methanol, acetronitrile, ethanol, and acetone.

Table 3.5 Possible compounds arising from the H_3O^+ precursor ion

Observed mass peak in SIFT spectrum	**Molecular Weight**	**Possible compounds**	**Chemical Formula**
19	18	Water	H_2O
37,55,73	36,55,72	Water Cluster	$[H_2O]n$
29	28	Ethylene	C_2H_4
31	30	Ethane	C_2H_6
	30	Formaldehyde	CH_2O
33, 51,69	32	Methanol	CH_3OH
42,60,78	41	Acetronitrile	CH_3CN
43	42	Propene	C_3H_6
	42	Cyclopropane	$c\text{-}C_3H_6$
45	44	Ethanal (Acetaldehyde)	C_2H_4O
	44	Propane	C_3H_8
47	46	Nitrogen dioxide	NO_2
47,65,83	46	Ethanol	C_2H_5OH
59	58	Butane	C_4H_{10}
59,77,95	58	Acetone	C_3H_6O
69	68	Isoprene	C_5H_8
71	70	2-Butenal	C_4H_6O
	70	Pentene	C_5H_{10}
	70	Cyclopentane	$c\text{-}C_5H_{10}$
	70	2-Pentene	C5H10
73	72	Pentane	C_5H_{12}
79	78	Benzene	C_6H_6
93	92	Toluene	C_7H_8

Observed mass peak in SIFT spectrum	**Molecular Weight**	**Possible compounds**	**Chemical Formula**
	92	Azulene	$C_{10}H_8$
95	94	2-Methylpyrazine	$C_5H_6N_2$
101	100	n-Hexanal	$C_6H_{12}O$
	100	3-Methyl hexane	C_7H_{16}
107	106	Xylene	C_8H_{10}

Table 3.6 the O_2^+ precursor ion reacts with Analytes

Analytes	**Molecular Weight**	**Product ion**	**Observed mass peak in SIFT spectrum**
Ammonia (NH_3)	17	NH_3^+	17
Ethylene (C_2H_4)	28	$C_2H_4^+$	28
Ethane (C_2H_6)	30	$C_2H_5^+$, $C_2H_6^+$	29,30
Methanol (CH_3OH)	32	CH_4O^+, $CH_3OH_2^+.H_2O$, $CH_3OH_2^+.2H_2O$	32, 51,69
Propene (C_3H_6)	42	$C_3H_6^+$	42
Cyclopropane (c-C_3H_6)	42	$C_3H_6^+$	42
Acetaldehyde (C_2H_4O)	44	CH_3CO^+ ,CH_3CHO^+	43,44
Ethanol (C_2H_5OH)	46	$C_2H_5O^+$, $C_2H_6O^+$	45, 46
Methane (CH_4)	47	$CH_3O_2^+$	47
Butane (C_4H_{10})	58	$C_4H_{10}^+$, $C_3H_6^+$ $C_3H_7^+$	42, 43,58
Acetone (C_3H_6O)	58	$CH_3COCH_3^+$	58
Propanol (C_3H_7OH)	60	$C_3H_7O^+$	60
Isoprene (C_5H_8)	68	$C_5H_8^+$	68

3.2.2 Moisture removal technique for HCO^+;

Because of the rapid reaction of the HCO^+ precursor ion with water, it was necessary to remove water from the samples. The method we chose was to use phosphorus pentoxide (P_2O_5) as a drying agent (dessicant). We achieved this by adding P_2O_5 to a glass tube container inserted in between the balloon and the capillary sampling inlet (see Figure 3.2).

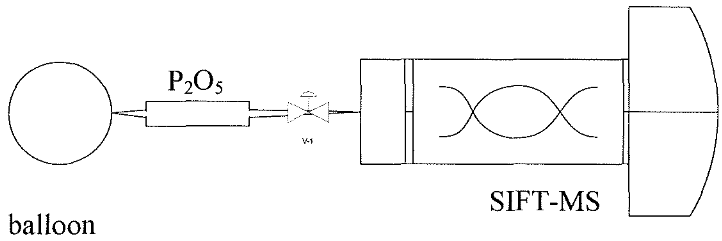


Figure 3.2 Diagram of Moisture Removal Chain.

3.2.3 Selection of precursor ions used in this study

As the O_2^+ precursor ion reacts efficiently with low proton affinity and high ionization potential molecules [Wilson et al, 2003], it has the following advantages over other precursor ions:

- it can identify all the small hydrocarbons except methane (although methane can also be detected at lower sensitivity from its slow reaction with O_2^+)
- The water cluster ions that occur with H_3O^+, are very small and do not complicate the analysis
- In addition to the hydrocarbons mentioned earlier, other analytes of interest include NO_2 and ammonia

An advantage of the H_3O^+ precursor ion is

- It transfers a proton to all molecules that have a proton affinity greater than H_2O.

- It generally yields only one primary product ion
- It detects efficiently other analytes of interest including acetaldehyde, acetone, ethanol, methanol and benzene

Its disadvantages are that it

- forms cluster ions with water and these complicate the analyses
- reacts slowly with small hydrocarbons

An advantage of the NO^+ precursor ion is that it can react with organic molecules via hydride ion (H^-) transfer and it reacts efficiently with some ketones by association.

The only significant advantage of the HCO^+ precursor ion is that it will identify SO_2 by proton transfer, which the other precursor ions cannot do. It does however suffer the serious disadvantage in that it rapidly transfers a proton to H_2O and thus very dry samples are required when it is used.

3.3 Air Samples Analyses in SIFT Laboratory

3.3.1 Sample storage

The sample balloons were labelled with the place and date of samples. The balloons were also kept away from direct sunlight and heat to avoid the development of undesired chemical reactions.

The samples were transported by car to the laboratory and stored at room temperature until the analysis process started.

3.3.2 Sample injection technique

The SIFT -MS instrument requires 2 hours for pre-conditioning. After this period has passed, the selected precursor ion signal was monitored for the amplitude and the instrument was calibrated for the mass. Air samples were drawn into the system through the heated capillary inlet to test the operation of the instrument (Figure 3.2). A 10 mm diameter PVC tube on the outlet of the capillary inlet was then inserted into the hole at the balloon stem. Contamination from laboratory air was avoided by maintaining a good fit between the balloon valve and the PVC tube. The air sample was then evacuated from the balloon through the capillary by the low pressure within the flow tube causing transfer of air from the balloon.

3.3.3 Result monitoring;

Three to five samples per balloon were analysed and the average signal count of products from the reaction of the selected precursor ion were recorded. From the signal counts, the concentration of each compound was calculated from the rate coefficient (k). Although a large numbers of VOCs can be observed in air using SIFT-MS, we decided somewhat arbitrarily to concentrate on nine of them only, as shown in Figure 4.1

Chapter 4 Results from Sampling

4.1 Variability of selected compounds during days and nights

As mentioned in the previous chapter, the samples outlined here were taken principally from 3 different sites, Hornby represents an industrial area, Riccarton is a site representative of high traffic density and St. Albans is representative of a residential area. Although quite a number of different volatile organic compounds (VOCs) were identified in Christchurch ambient air samples, it was decided to concentrate on the 9 volatile species identified in Figure 4.1 viz NH_3 (ammonia), C_2H_4 (acetylene), C_3H_6 (propene), CH_3OH (methanol), C_2H_5OH (ethanol), CH_3CHO (acetaldehyde), C_6H_6 (benzene), C_7H_8 (toluene) and C_8H_{10} (xylene) (see section 1.6).

The air samples, taken during winter and summer of 2002 for both day and night time, provide a clear data profile from each site (Figure 4.1). The number of sites for the summer samplings was extended over the three sites mentioned as discussed in section 4.1.3. It is evident that the two dominant compounds, C_3H_6 (propene) and C_2H_5OH (ethanol), have higher concentrations during the night time. Because there are two VOCs corresponding to the peak at m/z = 43 that was identified as C_3H_6 (propene) through proton transfer from H_3O^+, it was necessary to pay some attention to the kinetics of the species identified as C_3H_6 (propene). The other possible VOC is c-C_3H_6 (cyclopropane) that also exhibits a proton transfer peak at m/z = 43. The definitive means of distinguishing between them is by using NO^+ as the precursor ion. C_3H_6 (propene) only forms an adduct with NO^+ at m/z =72 whereas c-C_3H_6 (cyclopropane) exhibits charge transfer (see Table 3.3). Figure 4.2 shows a scan at the Riccarton site using an NO^+ precursor. A peak at m/z = 72 is clearly identified showing the identity of the proton transfer peak at m/z = 43 is propene and not c-C_3H_6 (cyclopropane). The presence of ethanol although unexpected was unambiguous. Ethanol is clearly identified from its proton transfer reactions with water. The appearance of the water cluster ions $C_2H_5OH_2^+.(H_2O)_n$ n=0-2 at m/z = 47, 47+18 and 47 + 36 are the tell tale product ions for C_2H_5OH (ethanol) (see Figure 3.1).

As there are large differences in concentration between propene and ethanol and the other compounds, it is necessary to magnify the scale as shown in Figure 4.3 which depicts these pollutants against the background of a Christchurch city map.

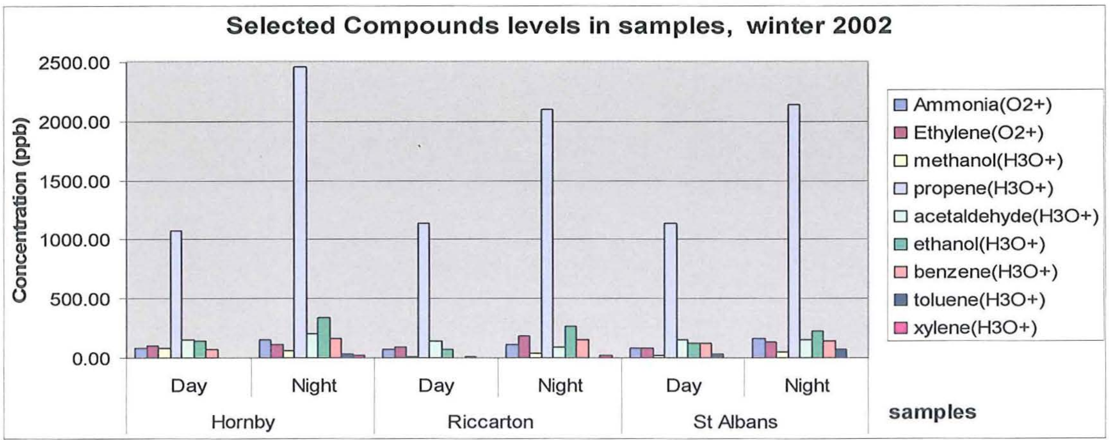


Figure 4.1 Change in profile of selected compounds with time during the winter. The results from each site are the averages of several samples taken on different days and nights.

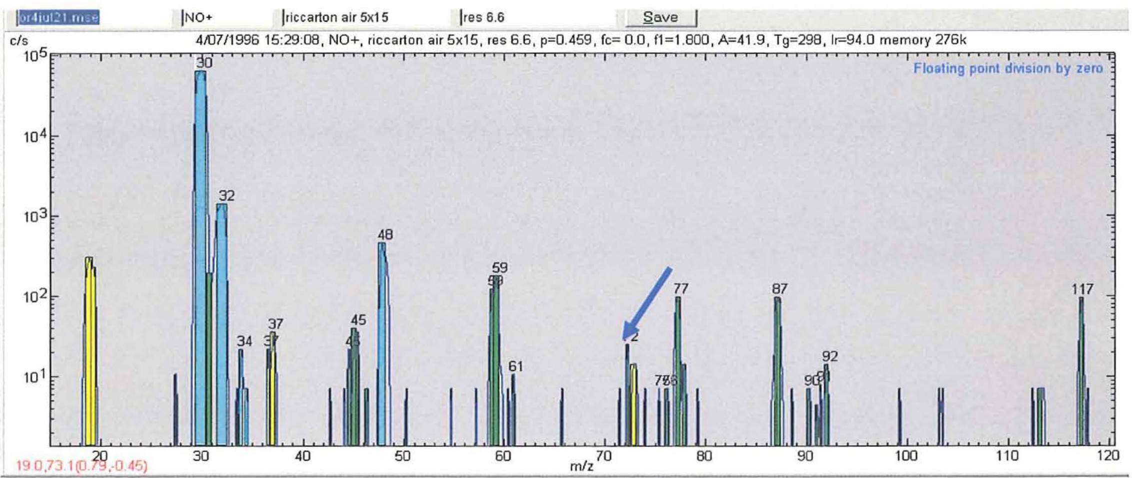


Figure 4.2 Mass spectrum of Riccarton air using an NO^+ precursor

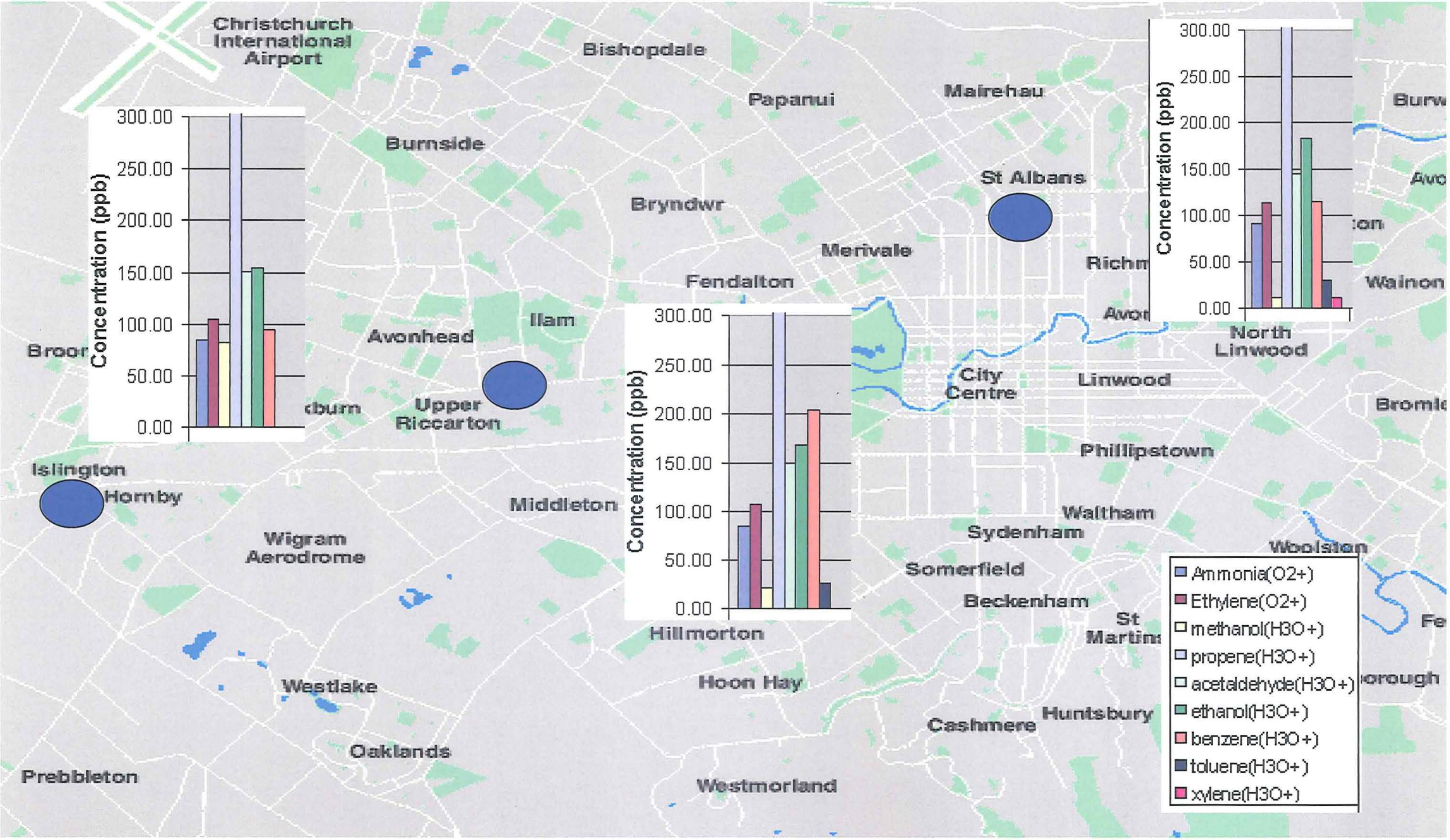


Figure 4.3 Concentrations of selected compounds from each site around city during winter days 2002

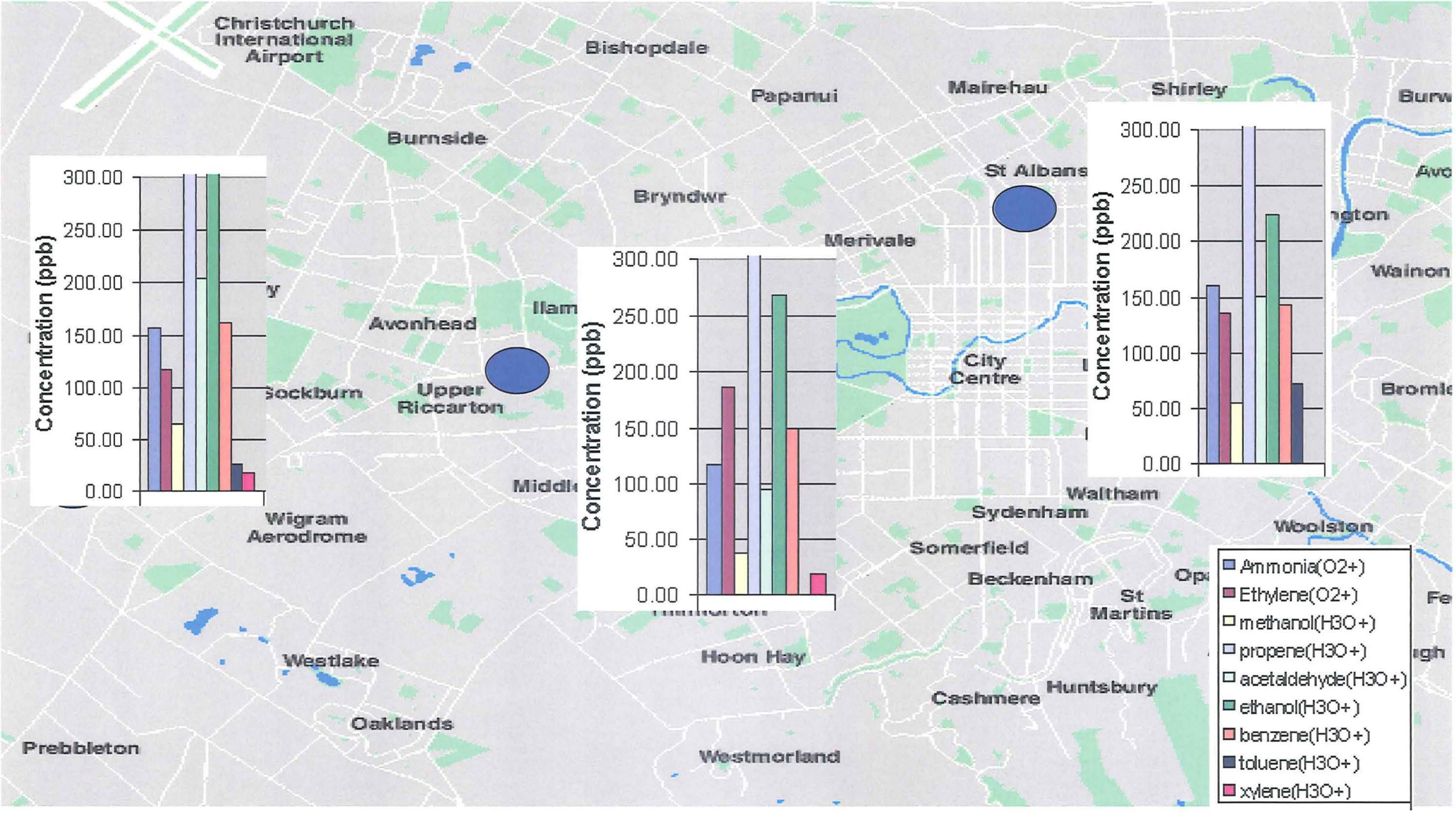


Figure 4.4 Concentrations of selected compounds from each site around city during winter nights 2002

4.1.1 Winter daytime

The day time samples were taken in the morning after the rush hour during weekdays and weekends from the selected sites. The samples were obtained in a random fashion: some days before nights exhibiting a high degree of pollution and sometimes on days immediately following nights of high pollution. The results shown in Figure 4.1 and 4.3 are the average of 6 measurements taken on different days.

1) Hornby site

From Figure 4.1 and 4.3, the C_3H_6 (propene) concentration is noticeably the highest among those selected compounds in this location, followed by C_2H_5OH (ethanol) and CH_3CHO (acetaldehyde) at much lower concentrations. C_6H_6 (benzene), NH_3 (ammonia), CH_3OH (methanol), and C_2H_4 (ethylene) are also detected at significant levels in all the samples. At the levels observed, it is most likely that the compounds originate from anthropogenic sources, such as vehicle combustion or industrial processes located in this area.

C_7H_8 (toluene) and C_8H_{10} (xylene) were not present in the samples from this site. These compounds are known to be common VOCs in urban areas, but not industrial areas. [Mohamed et al, 2002]

2) Riccarton site

As with the Hornby site, the C_3H_6 (propene) level is also present at the highest concentration. The concentration of CH_3CHO (acetaldehyde) appeared to be greater than C_2H_5OH (ethanol), NH_3 (ammonia) and C_2H_4 (ethylene), respectively. Trace amounts of C_7H_8 (toluene) and methanol (CH_3OH) were found in samples from this site.

At this site neither C_6H_8 (benzene) nor C_8H_{10} (xylene), which are commonly found in urban areas were observed. This is counter to expectation since the traffic density was quite high when the samples were taken. Weather conditions at times were no wind; sunny, warm temperatures, and moderate humidity.

3) St. Albans site

As with the previous two sites, the C_3H_6 (propene) concentration is the highest, followed by CH_3CHO (acetaldehyde) with slightly higher concentrations than C_2H_5OH (ethanol), and C_6H_6 (benzene). C_6H_6 (benzene) was at higher concentrations at the St. Albans site than the high traffic area, Riccarton site. NH_3 (ammonia) and C_2H_4 (ethylene) concentration levels were also significant. Small amounts of C_7H_8 (toluene) and CH_3OH (methanol) were also found in these samples. Weather conditions were; sunny, clear sky and warm morning wind (Appendix A, B and C).

4.1.2 Winter nighttimes

Normally, during the winter nights, the selected compounds were found at noticeably higher detectable levels than those during the day samples. However, the samples from the three sites present quite distinctly different data (Figure 4.1 and 4.4).

1) Hornby site

The results from this site share some common factors with the other two sites. C_3H_6 (propene) was present at the highest concentration levels even though the temperature is lower during the nights. The concentration of C_3H_6 (propene) found at this site at night was the highest (2,458 ppb) of all contaminants found in this investigation. All the selected compounds were found in the samples at detectable levels.

Night concentrations of C_6H_6 (benzene), C_2H_5OH (ethanol), NH_3 (ammonia), CH_3CHO (acetaldehyde) and C_2H_4 (ethylene) were all greater than day samples. In contrast, the CH_3OH (methanol) concentration was lower than in the day samples. Although C_7H_8 (toluene) and C_8H_{10} (xylene) were not detected during the day, they were present in the night samples in trace amounts from this site.

2) Riccarton site

C_3H_6 (propene) is the dominant species, followed by C_2H_5OH (ethanol) and C_6H_6 (benzene). These species are likely contributions from the traffic as they are components of petrol. It is surprising that C_6H_6 (benzene) and C_8H_{10} (xylene) are only present in the night air samples from this site, however, C_7H_8 (toluene) concentrations were not at detectable levels. While the other compound levels drastically increased during the night at this traffic area, the CH_3CHO (acetaldehyde) concentration exhibited a noticeable reduction in level. This may be an indication of at least some photochemical component for CH_3CHO (acetaldehyde).

3) St. Albans site

The results for this site show that all the compounds of interest were detected with the exception of C_8H_{10} (xylene). As in the other sites, the concentration of propene is much higher than other detected pollutants. The compounds of interest present at different concentrations, with ranking from high to low were: C_2H_5OH (ethanol), NH_3 (ammonia), CH_3CHO (acetaldehyde), C_6H_6 (benzene), C_2H_4 (ethylene), C_7H_8 (toluene), and CH_3OH (methanol). The trend of larger concentrations of volatiles at night than the concentrations during the day is continued here. C_7H_8 (toluene) showed the highest average concentration (72 ppb) of all the sites and times.

4.1.3 Summer daytime

There were many more sites sampled in the summer period in addition to the sites reported in sections 4.1.1 and 4.1.2. The summer samples were made from nine sites around the city. It is evident from the results that for some selected compounds, concentrations appear at higher levels in the traffic congestion areas. The results for all the summer sites are summarized in Figure 4.5 and 4.6. Each graph for day and night is the average of three measurements.

1) Hornby site

Among the compounds present in the samples from this site, C_2H_5OH (ethanol) concentration is highest, exceeding even the C_3H_6 (propene) levels. The observed analytes examined from high to low concentrations are as follows; C_2H_5OH (ethanol), C_3H_6 (propene), CH_3CHO (acetaldehyde), NH_3 (ammonia), C_7H_8 (toluene), C_6H_6 (benzene), CH_3OH (methanol), and C_8H_{10} (xylene). Surprisingly, C_2H_4 (ethylene) was not detected.

2) Riccarton site

Every compound of interest was present, and again the summer trend was followed with C_2H_5OH (ethanol) being slightly higher than C_3H_6 (propene). These two volatiles are at much greater levels than the other seven. Furthermore, the C_2H_5OH (ethanol) level at this site was the highest among all the samples (1,494 ppb). It is interesting to note that the samples taken during the weekend exhibited higher concentrations of C_2H_5OH (ethanol) and C_3H_6 (propene) compared with samples taken during weekdays. To put the amounts of C_2H_5OH (ethanol) observed into perspective, the C_2H_5OH (ethanol) levels in human breath after a single 7 oz beer are in excess of 5 ppm.

3) St. Albans site

Surprisingly, C_7H_8 (toluene) was not detected in the day time samples. On the other hand, the C_2H_5OH (ethanol) concentrations were the highest with C_3H_6 (propene) ranked the second, followed by CH_3CHO (acetaldehyde), NH_3 (ammonia), and CH_3OH (methanol). There were also low levels of C_2H_4 (ethylene) and C_8H_{10} (xylene) at this site. The profile of the selected compounds is not significantly different from the samples at the previous sites. The average concentration of C_8H_{10} (xylene) at this site was observed at the highest (40 ppb) levels of all sites examined. (Figure 4.6)

4) Corner of Deans Road and Riccarton Road

Even though this site is next to a recreation area, Hagley Park, it is one of the busiest intersections in Christchurch. C_2H_5OH (ethanol) and C_3H_6 (propene) were dominant in the samples, CH_3CHO (acetaldehyde) and NH_3 (ammonia) were present at significant similarl concentration levels. The aromatic VOCs common to urban areas, namely, C_6H_6 (benzene), C_7H_8 (toluene), and C_8H_{10} (xylene) were detected at trace amounts. It may be assumed that these pollutants originate from combustion engines.

5) Corner of Clyde Road and Memorial Avenue

Low concentrations of NH_3 (ammonia), C_2H_4 (ethylene), CH_3CHO (acetaldehyde), and C_6H_6 (benzene) were present while C_7H_8 (toluene) and C_8H_{10} (xylene) appeared at trace concentrations for this site.

Similar to other sites, the two dominant compounds are C_2H_5OH (ethanol) and C_3H_6 (propene).

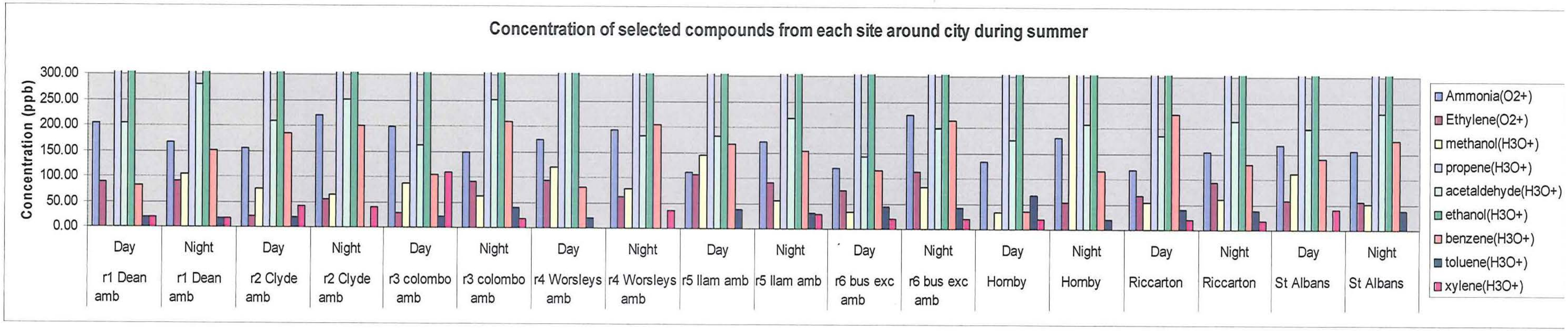


Figure 4.5 Summer day and night results for the nine sites.

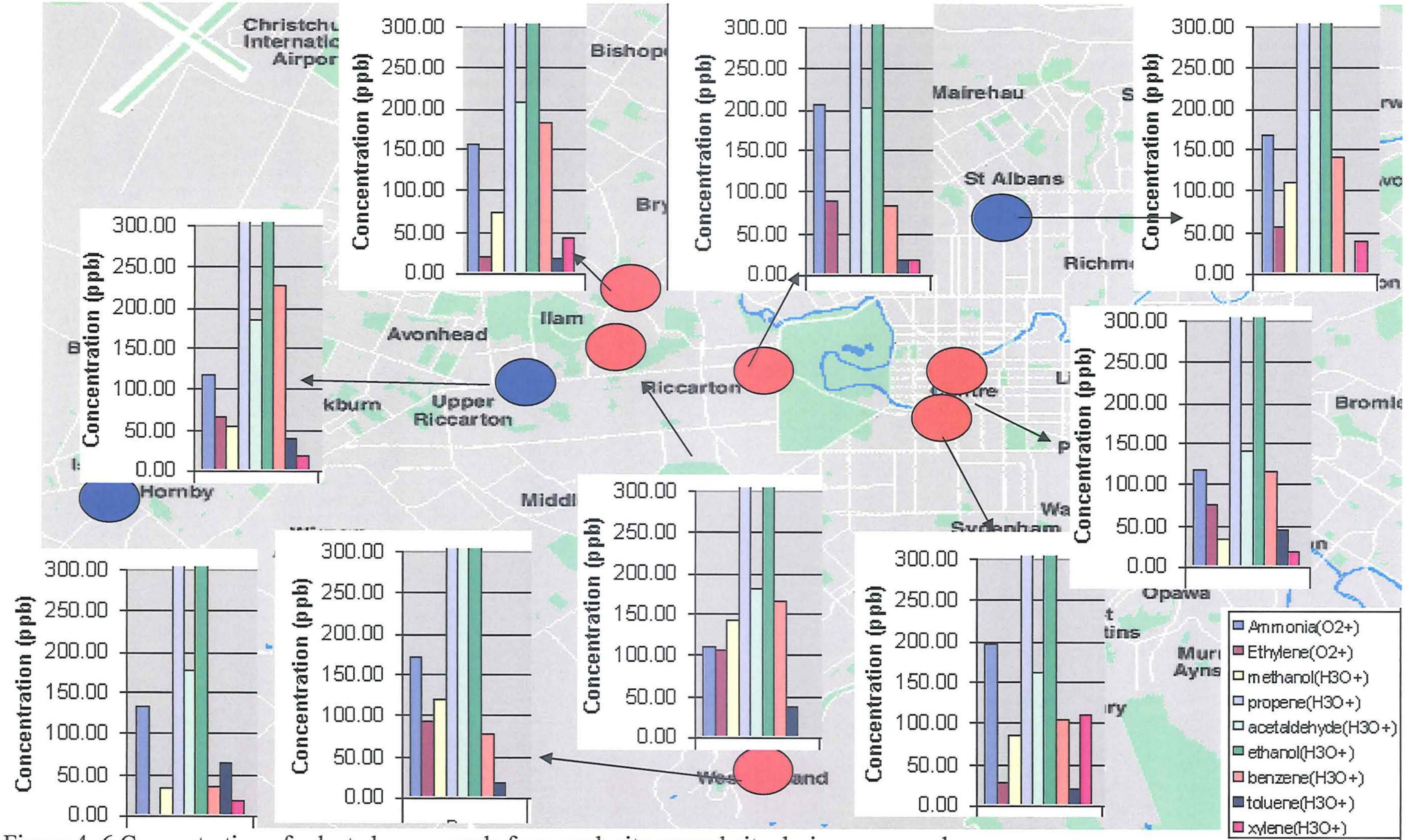


Figure 4 .6 Concentration of selected compounds from each site around city during summer days

6) Corner of Colombo Street and Moorhouse Avenue

This site is located at one of the busiest intersections of the city, however, the data profile shows similarity to samples from other sites in that all the selected compounds were detected in the samples. The selected compounds present ranked from high concentration to low are: C_2H_5OH (ethanol), C_3H_6 (propene), NH_3 (ammonia), CH_3CHO (acetaldehyde), C_8H_{10} (xylene), C_6H_6 (benzene), CH_3OH (methanol), C_2H_4 (ethylene), and C_7H_8 (toluene).

7) Worsleys Road

C_2H_5OH (ethanol) was present at higher concentration levels than C_3H_6 (propene), followed by CH_3CHO (acetaldehyde), NH_3 (ammonia) and C_6H_6 (benzene) at similar concentrations. The VOCs common to urban areas, namely, C_7H_8 (toluene) at very low concentration and C_8H_{10} (xylene) were present in the samples from this site. It is remarkable that these compounds have concentrations similar to other sites. These results were unexpected as this site was anticipated to be more representative of background ambient air of the city as it is further away from many anthropogenic activities. See section 4.1.4 for comments on this site.

8) Corner of Ilam Road and Riccarton Road

CH_3CHO (acetaldehyde), and C_6H_6 (benzene) were detected at significant levels. Also C_7H_8 (toluene) was present in trace amounts. This site is quite close to the Ricarton site, so the VOC concentration profiles at the two sites might be expected to be similar as was observed.

9) Bus exchange centre

All compounds of interest are present in the samples from this site. Concentrations of C_2H_5OH (ethanol) and C_3H_6 (propene) are also similar to the other samples. Other detected compounds from high to low concentrations were: CH_3CHO (acetaldehyde), NH_3 (ammonia), C_6H_6 (benzene), C_2H_4 (ethylene), CH_3OH (methanol), C_7H_8 (toluene) and C_8H_{10} (xylene). As with most of the sites examined, there is a great disparity between the concentrations of the two dominant compounds (~ 800- 1100 ppb) and the remainders (less than ~20-140 ppb).

4.1.4 Summer nighttimes

The results of air samples that were taken during summer nights show a clear data profile from each site (Figure 4.7). As with the daytime samples, C_2H_5OH (ethanol) concentrations are the highest of all VOCs on summer nights, at all sites. It is interesting to note that the samples from the corner of Ilam road and Riccarton road contained the highest levels of this compound.

<u>1) Hornby site</u>

Similar to all other sites, the two dominant compounds are C_3H_6 (propene) and C_2H_5OH (ethanol) (> 1,000 ppb) as in the day time. The compounds present at low concentrations are CH_3OH (methanol), CH_3CHO (acetaldehyde), NH_3 (ammonia), C_6H_6 (benzene), C_2H_4 (ethylene) and C_8H_{10} (toluene). It should be noted that in the night time samples, the concentrations of CH_3OH (methanol) greatly increased over the day samples from this site.

<u>2) Riccarton site</u>

Small amounts (< 100 ppb) of C_8H_{10} (xylene), C_7H_8 (toluene), CH_3OH (methanol) and C_2H_4 (ethylene) were detected. Also NH_3 (ammonia), CH_3CHO (acetaldehyde), and C_6H_6 (benzene) were present at higher concentrations. The levels of C_3H_6 (propene) and C_2H_5OH (ethanol) were much higher than the other selected VOCs, and were similar to other summer samples. It is noticeable that the concentrations of the compounds of interest showed only slightly differences between day and night samples.

3) St. Albans site

The results obtained showed that C_2H_5OH (ethanol) concentrations were also highest, followed by C_3H_6 (propene) and from all observations this now appears to be common behaviour for most summer time sites in Christchurch. The remaining VOCs were CH_3CHO (acetaldehyde), C_6H_6 (benzene), and NH_3 (ammonia). Smaller amounts of C_2H_4 (ethylene) and C_7H_8 (toluene) were found at low concentrations in this sample, while C_8H_{10} (xylene) was not detected.

4) Corner of Deans Road & Riccarton Road

The common VOCs in urban areas arising from fuel combustion, namely, C_6H_6 (benzene), C_7H_8 (toluene), and C_8H_{10} (xylene) were present at significant concentration levels. Besides the dominant C_3H_6 (propene) and C_2H_5OH (ethanol) VOCs, significant levels of the other compounds were found. Low concentrations of CH_3OH (methanol) were present in the night time samples but not in the day samples.

5) Corner of Clyde Road & Memorial Avenue

It is clear that the concentration profiles of selected compounds are similar to other sample sites except that C_7H_8 (toluene) was not detected. Concentrations of NH_3 (ammonia) were detected at similar levels to those present in samples from the bus exchange. C_2H_4 (ethylene), CH_3OH (methanol), and C_8H_{10} (xylene) appeared at trace amounts. As always in summer sites, ethanol was present at the highest concentrations followed by C_3H_6 (propene) and CH_3CHO (acetaldehyde).

6) Corner of Colombo street & Moorhouse Avenue

The concentration ranking is quite different to the day time for this site. CH_3CHO (acetaldehyde), C_6H_6 (benzene) and C_2H_4 (ethylene) are significantly higher in the day samples, and the C_7H_8 (toluene) amount is slightly increased. In contrast, the NH_3 (ammonia), CH_3OH (methanol), and C_8H_{10} (xylene) levels are lower in the night samples.

7) Worsleys Road

The profile of the night time samples of the selected compounds is similar to the day time samples. C_2H_5OH (ethanol) was present at higher concentration levels than C_3H_6 (propene), while NH_3 (ammonia), CH_3CHO (acetaldehyde), and C_6H_6 (benzene) appeared at similar concentrations. In addition, C_8H_{10} (xylene) was at the lowest levels of all the compounds of interest. This site was used as representative of the background ambient air of Christchurch since it is surrounded by farms and is close to uninhabited hilly terrain, without a lot of anthropogenic activities. It was interesting to note that NH_3 (ammonia), C_2H_5OH (ethanol), and C_6H_6 (benzene) concentrations were higher in the night samples than the day samples. From these results, it is also evident that C_8H_{10} (xylene) was present only in the night samples from this site, while toluene appeared only in the day samples.

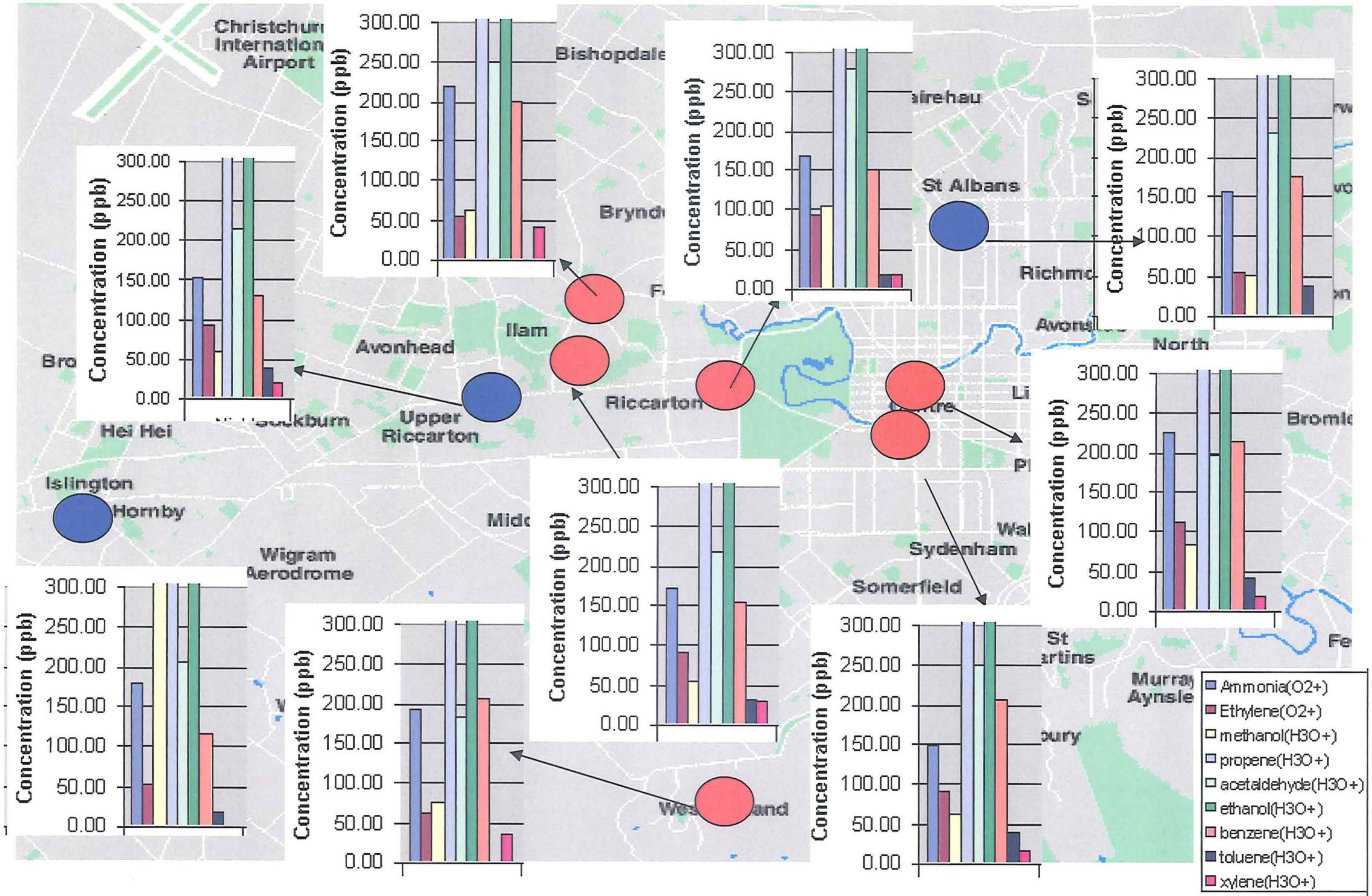


Figure 4 .7 Concentration of selected compounds from each site around city during summer nights

8) Corner of Ilam Road and Riccarton Road

CH_3OH (methanol) concentration appeared at lower levels in the day time samples. However, for this site the day-night variation is significantly greater compared to samples from the Riccarton site (day/night). In contrast to the results obtained from the Ricarton site, the C_6H_6 (benzene) levels did not change appreciably between day and night samples.

9) Bus exchange centre

As with all the other summer sites, C_2H_5OH (ethanol) and C_3H_6 (propene) were present at the highest levels of the selected compounds followed by CH_3CHO (acetaldehyde), NH_3 (ammonia) and C_6H_6 (benzene) which were present at similar concentrations. CH_3OH (methanol), C_7H_8 (toluene) and C_8H_{10} (xylene) appeared at trace concentrations in this sample.

4.1.5 MUI files

As mentioned in Chapter 3 there are two different modes of operation in the SIFT-MS technique: mass scan mode and selected multi ion (MUI) mode. The previous sections show data from the first mode of operation; mass scan mode. Nevertheless, this study also used the latter mode for trips 4, 6 and 7. While the results in the MUI mode exhibit more accuracy than the full scan mode they are only relevant to the VOCs selected for study.

The MUI studies in this work were directed at monitoring only four VOCs: CH_3OH (methanol), CH_3CHO (acetaldehyde), C_6H_6 (benzene) and C_7H_8 (toluene) (Figure 4.8).

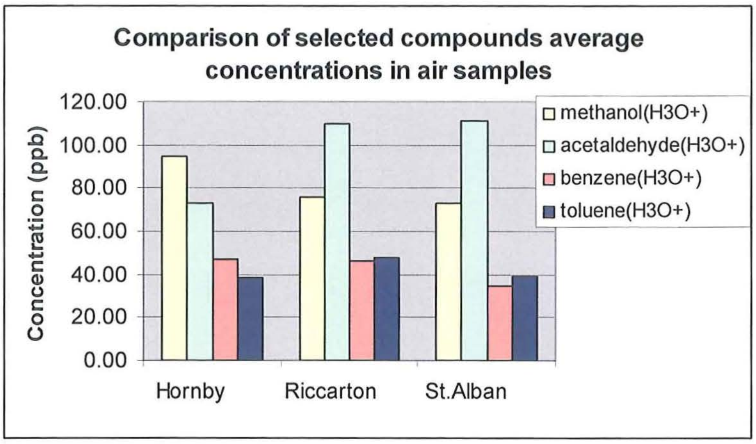


Figure 4.8 Comparison of selected compounds average concentrations in air samples from winter nights 2002, using multi ion mode of analysis.

Although the MUI mode of operation only displays data for the analytes selected, the data is inherently more accurate than from the mass scan mode. A further advantage is that in the MUI mode only very small volume samples are required and these are processed within a few seconds. Whereas a full mass scan is typically averaged over 20 seconds.

From other research for urban ambient air in USA, Mexico and Hong Kong, the level of C_7H_8 (toluene) is much higher (3 - 8 times) than C_6H_6 (benzene) levels [Mohamed et al, 2002, Ortiz et al, 2002 and Lee at el, 2002]. Unlike their results, the samples from Christchurch air show the levels of these compounds to be quite different and this may reflect the characteristics of gasoline refined for the New Zealand situation. Furthermore, the data for the mass scan mode also shows that concentrations of C_6H_6 (benzene) are much greater than (2 - 5 times) C_7H_8 (toluene) concentrations. These data are the averaged results of day and night samples for both winter and summer.

C_6H_6 (benzene) can be contributed from traffic, according to the automobile combustion efficiency. The composition of vehicle emissions plays the major role in determining ambient VOC pollution in the city area. Other factors that influence the VOC emissions are the New Zealand petrol composition which is quite different from other countries, as well as the type of cars. Regulations in New Zealand on cars performance are not strict and a high percent of cars on the road are second hand imports from Japan. Photochemistry reaction is also another factor. For instance, CH_3CHO (acetaldehyde) is a precursor to peroxyacetyl nitrate (PAN) which is produced only from photochemical reaction [Jacobson, 2002]. The reaction pathway is

$$CH_3CH(=O)(g) + \dot{O}H(g) \rightarrow CH_3\dot{C}(=O)(g) + H_2O(g) \qquad \ldots.4.1)$$

Acetaldehyde	Hydroxyl radical	Acetyl radical	water vapour

$$CH_3\dot{C}(=O)(g) + O_2(g) \xrightarrow{M} CH_3C(=O)\dot{O}_2(g) \qquad \ldots.4.2)$$

Acetyl radical	Molecular oxygen	Peroxyacetyl radical

$$CH_3C(=O)\dot{O}_2(g) + \dot{N}O_2(g) \overset{M}{\rightleftarrows} CH_3C(=O)(g) \qquad \ldots.4.3)$$

Peroxyacetyl radical	Nitrogen dioxide	Peroxylacetyl nitrate (PAN)

where M is an inert molecule such as N_2. Reaction 4.3) is reversible, and strongly temperature dependant. For example at 300 K, PAN's life time is about 25 minutes whereas at 280 K its life time becomes 13 hours at the same pressure [Jacobson, 2002]. The peroxylacetyl radicals from this reaction also convert NO (nitric oxide) to NO_2 (nitrogen dioxide). Nitrogen dioxide photolysis results in O_3 (ozone) formation in the troposphere. Another pathway for O_3 (ozone) formation is photolysis of CH_3CHO (acetaldehyde).

$$\underset{\text{Acetaldehyde}}{CH_3CHO\,(g)} \quad + h\nu \quad \rightarrow \quad \underset{\text{Methyl Radical}}{\overset{\bullet}{C}H_3\,(g)} \quad \underset{\text{Formyl radical}}{+H\overset{\bullet}{C}O\,(g)} \qquad \ldots.4.4)$$

Both products from this reaction, methyl radicals and formyl radicals are precursors to ozone formation. An unknown factor in the photolysis equation is the influence of the increase in solar UV radiation during late spring and early summer. New Zealand is exposed to extraordinary high levels of UV radiation due to its close proximity to the Antarctic, stratospheric O_3 (ozone) hole area.

4.2 Comparison of selected compounds between winter and summer

Although the spatial distribution of selected sites sampled in this study is not a statistically significant sample of urban locations in Christchurch, the results from these sites may indicate certain air quality trends that are common to the city atmosphere at the average height for inhalation (1.5 m above ground level).

Mohamed et al (2002) found from a study of VOCs in US urban areas, that the correlation between car ownership and HC concentrations in ambient air is not necessarily significant. There were however, some coincidences. For instance, the highest detected concentration of the total HCs and the second highest ownership data were found at the same monitored area.

They also found that VOCs generally have negative correlations with temperature as the VOCs clearly have a larger effect in summer. A further complication in Christchurch is that in winter there is a large contribution to pollution from home heating sources (ECan, 2002). The large PM10 component provides a significant potential for heterogeneous chemistry.

In this study, the seasonal averages of VOCs were based on samples collected during winter and summer from three sites; Hornby, Ricarton and St. Albans during July 2002 to February 2003. The samples were measured both during the day and the night at each site. The total number of samples at each site totals six per season. In two seasons twelve samples were analysed per site using the full scan mode of operation.

Table 4.1 Average concentrations of selected VOCs in winter and summer samples

VOCs	Hornby		Riccarton		St. Albans	
	Winter	Summer	Winter	Summer	Winter	Summer
Ammonia	121±98	157±62	104±68	135±78	123±68	162±35
Ethylene	111±60	27±65	150±170	80±42	122±57	56±44
Methanol	74±69	173±291	24±28	57±19	38±43	81±73
Propene	1,769±1,865	946±280	2,594±2,269	1,189±374	1,968±1,560	1,013±218
Acetaldehyde	177±205	191±67	119±163	200±31	150±187	214±95
Ethanol	245±134	1,403±268	225±101	1,493±286	196±51	1,382±168
Benzene	128±119	76±97	132±173	178±121	173±130	158±115
Toluene	13±32	43±53	15±23	39±30	49±64	19±29
Xylene	9±22	10±25	14±23	20±30	0±0	20±31

Table 4.1 shows the winter-summer average concentration of selected compounds. Summer concentrations were generally higher for NH_3 (ammonia), CH_3OH (methanol), CH_3CHO (acetaldehyde), C_2H_5OH (ethanol), and C_8H_{10} (xylene). In addition, there is only a slight difference in the concentration ratios (winter/summer) of those compounds in the samples from all sites. It is noted that the samples were taken under different environmental conditions and there were strong diurnal and seasonal variation in concentrations of these compounds, resulting in large variations of the data.

This result shows that the spatial variation of those compound concentration ratios between Hornby, Riccarton and St. Albans is small compared to seasonal variation. It is interesting to note that only C_3H_6 (propene) and C_2H_4 (ethylene) concentrations are higher in the winter samples from all sites. Further, the winter/summer ratio for C_6H_6 (benzene) is greater than 1 only at the Hornby site, while the same is true for C_7H_8 (toluene) only at the St. Albans site.

There are several factors that may affect the concentrations of the selected compounds in winter and summer, as mentioned previously in section 2.4 on meteorological conditions. If we ignore possible differences in anthropogenic activities between winter and summer then we may attribute seasonal variation of the data to meteorological differences. Possible influences include rainout of pollution and wind dispersion. In addition, photolytic chemistry can influence the variation of concentrations with season. Among the selected compounds in Table 4.1 there are distinct seasonal differences for C_2H_4 (ethylene), C_3H_6 (propene), C_2H_5OH (ethanol) and CH_3OH (methanol) across all sites. Figure 4.9 below shows the pronounced seasonal variations of C_3H_6 (propene) and C_2H_5OH (ethanol) concentrations. These two VOCs of interest are present at very high levels in the samples. At most sites they are present at higher concentrations in the night time samples during both winter and summer. It is also evident that C_3H_6 (propene) concentrations are higher during the winter nights. In contrast, C_2H_5OH (ethanol) levels are higher than C_3H_6 (propene) levels during the summer nights. These results are striking, unexpected and reproducible. C_2H_5OH (ethanol) has not been widely reported as a pollutant species in the literature but the application of this new technique of SIFT-MS to atmospheric environmental studies raises new and interesting environmental issues.

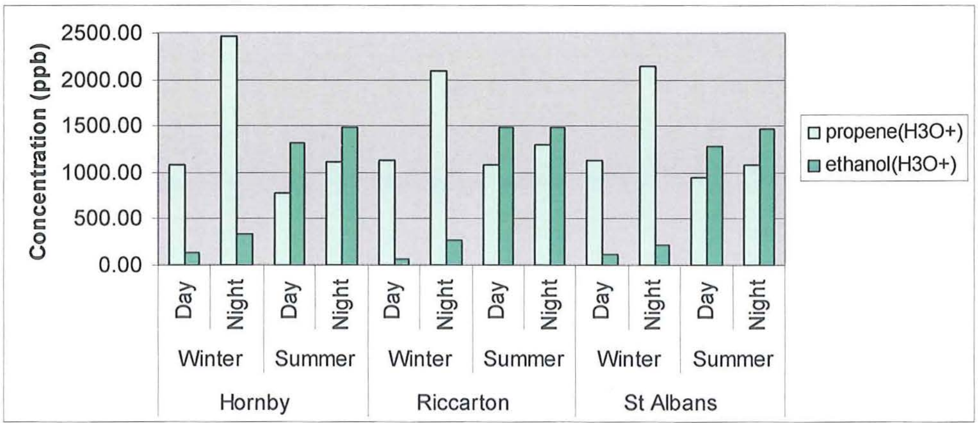


Figure 4.9 Comparison concentrations of propene and ethanol from winter and summer samples.

Ozone formation can occur as a consequence of chain reactions between C_3H_6 (propene) and OH (hydroxyl) radicals (Wayne, 2000) as

$$\overset{\bullet}{OH} + CH_3CHCH_2 \rightarrow \overset{\bullet}{CH_3CHCH2OH} \quad \ldots .4.5)$$

Hydroxyl radical   propene

Based on this reaction, the atmospheric lifetime of C_3H_6 (propene) is approximately 13 hours (Atkinson, 1994). Thus, it is possible that the longer days during the summer period lead to a reduction of C_3H_6 (propene) levels.

4.2.1 Ambient air from site

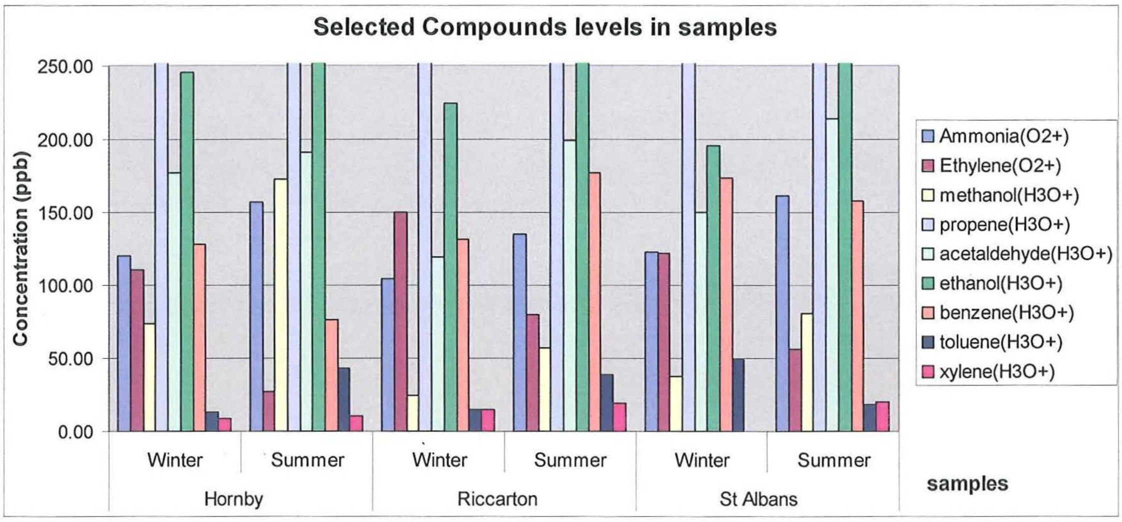


Figure 4.10 Comparison of selected compound concentrations in winter and summer samples.

1) Hornby site

The two compounds that dominated the observed VOCs are C_2H_4 (ethylene) and C_2H_5OH (ethanol). At this site, the level of C_2H_5OH (ethanol) is almost 5 times higher in summer samples. Nevertheless, it is clear that the concentration of C_2H_4 (ethylene) is more than 4 times higher in winter samples than summer at this site, followed by C_3H_6 (propene) and C_6H_6 (benzene) . There is little variation in concentration of CH_3CHO (acetaldehyde) in summer and winter samples while this component is slightly higher in summer samples at other sites.

2) Riccarton

This was the only site where concentrations of C_2H_4 (ethylene) and C_3H_6 (propene) measured higher in winter samples. In contrast to St. Albans but similar to Hornby, the concentration of toluene at the Riccarton site is more than 5 times higher than in summer samples. This also shows the largest difference in concentrations of ethanol between summer and winter samples. The seasonal differences observed at the Riccarton site are even greater than those from St. Albans and Hornby sites. The Riccarton site has the highest traffic density and a possible explanation for the higher summer C_2H_5OH (ethanol) levels observed, is that the traffic density may be higher in the summer.

3) St. Albans

It is clear that C_2H_4 (ethylene), C_3H_6 (propene) and C_7H_8 (toluene) concentrations are higher in the winter samples from this site. In contrast the NH_3 (ammonia), CH_3OH (methanol), CH_3CHO (acetaldehyde), and C_6H_6 (benzene) levels are significantly higher in the summer samples.

The levels of C_2H_5OH (ethanol) present in summer was almost 8 fold its concentration in winter samples. This site is mainly a residential area.

Furthermore, C_8H_{10} (xylene) which was not present at detectable levels in winter samples appeared at similar levels to toluene in summer samplings from this site.

4.3 Overall Representation summary

4.3.1 Winter results

As mentioned in Chapter 2 the three selected sites; Hornby, Riccarton and St. Albans are representative of industrial, traffic and residential areas, respectively. The concentration range of each selected compound is illustrated in Table 4.2. The selected compound concentrations in the samples occur at higher levels in the night samples from all sites, with the exception of CH_3CHO (acetaldehyde) from the Riccarton site and C_6H_6 (benzene) from the St. Albans site. Also C_7H_8 (toluene) and C_8H_{10} (xylene) are small and variable. The levels of all selected compounds ranked from high to low are as follows; C_3H_6 (propene), C_2H_5OH (ethanol), CH_3CHO (acetaldehyde), C_6H_6 (benzene), C_2H_4 (ethylene), NH_3 (ammonia), CH_3OH (methanol), C_7H_8 (toluene), and C_8H_{10} (xylene).

Table 4.2 The concentration range of selected compounds in air samples from winter 2002

Compounds	Average Concentration Range	
	ppb	$\mu g/m^3$
Ammonia	83 – 160	57 – 110
Ethylene	104-186	118 – 181
Methanol	11-83	14 – 107
Propene	1079-3085	1829 – 5230
Acetaldehyde	93-203	165 – 361
Ethanol	154-336	286 – 624
Benzene	94-204	296 – 642
Toluene	0-72	0 – 267
Xylene	0-18	0 – 77

4.3.2 Summer result

The levels of each VOC in summer samplings vary both by time and place. This can be related to the local anthropogenic activities and local micro environment.

The levels of all selected compounds ranked from high to low are as follows; C_2H_5OH (ethanol), C_3H_6 (propene), CH_3CHO (acetaldehyde), NH_3 (ammonia), C_6H_6 (benzene), C_2H_4 (ethylene), CH_3OH (methanol), C_7H_8 (toluene), and C_8H_{10} (xylene) (Table 4.3).

Table 4.3 The concentration range of selected compounds in air samples from summer 2002

Compounds	Average Concentration Range	
	ppb	$\mu g/m^3$
Ammonia	117 – 179	80 – 123
Ethylene	0 – 92	0 – 104
Methanol	33 – 313	43 - 404
Propene	780 – 1303	1322 - 2209
Acetaldehyde	176 – 230	313 - 408
Ethanol	1286 – 1494	2388 - 2774
Benzene	35 – 226	110 - 711
Toluene	0 -65	0 - 241
Xylene	0 – 40	0 - 171

Meteorological concerns

According to the ECan data, during high pollution nights (3/7/02 PM_{10} = 156 $\mu g/m^3$ and 9/7/02 =68 $\mu g/m^3$) [ECan, 2002], the concentrations of the VOCs selected for this study are higher than the levels during the low pollution nights.[appendix E] It was observed that the concentrations of the compounds of interest correlate with the level of PM_{10} in the air and the weather conditions. The wind and topography of Christchurch in the morning following a temperature inversion, disperses pollutants away from the city. In accordance, our observations generally support the influence of meteorology in that the concentrations of the trace VOCs as measured from the night samples dropped sharply in the following day.

4.4 Conclusion

SIFT-MS technology has enabled rapid identification of trace VOCs in the environment. That this pilot study of VOCs in the ambient air of Christchurch had quite unexpected findings, merely serves to illustrate the effectiveness of this analytical technique.
The maximum concentration of selected compounds varies as shown in Table 4.4 which also includes the period and place the sample was taken. It should be noted that all the samples were taken during times of high pollution. The samples were obtained during traffic rush hours (8.30 - 11.0 am) for day samples and after dinner (8.30 - 11.00 pm) for night samples. As a consequence, the results from this study mainly portray the concentrations of selected compounds at high pollution periods. The result of large variation in these VOCs concentrations (i.e. the standard deviations) is due to the varying pollution levels at different times, dates and places.

Table 4.4 Maximum concentration of selected compounds in air samples

Compounds	Sample Site	Date (dd/mm/yy)	Time	WHO Guidelines ($\mu g/m^3$)	Concentration /[a] (ppb) (avg 3 trips/time)
Propene	Hornby	03/07/02	Night	n/a	3671 (2458 ± 2030 SN)
Ethanol	Bus Exchange	15/12/02	Day	n/a	1949 (1494 ± 305 SD)
Methanol	Hornby	9/12/02	Night	n/a	762 (313 ± 391 SN)
Acetaldehyde	Worsleys	16/12/02	Day	5	642 (230 ± 89 SN)

Ethylene	Riccarton	03/07/02	Night	n/a	414 (186 ± 209 WN)
Benzene	Riccarton	03/07/02	Night	5-20	358 (226 ±130 SD)
Ammonia	Colombo	16/12/02	Day	n/a	315 (179 ± 43 SN)
Xylene	Colombo	13/02/03	Day	1-100	168 (40.3 ± 34 SD)
Toluene	Riccarton	21/7/02	Night	5-150	160 (72 ± 81WN)

S=summer, W=winter, Day=day sample, N=night sample

/[a] The maximum concentration in ppb of each volatile is shown. The average value of all the measurements is shown in the parenthesis.

Some of the compounds monitored may have a clearly identified source of origin. For example, industrial accidents can contribute to NH_3 (ammonia) in the industrial area since there have been several big leakages of this gas recorded in the past [The Press, 12/4/91, 26/6/99, 23/5/02]. Smaller leakages might not be noticed and therefore not be reported.

It is clear that C_3H_6 (propene) and C_2H_5OH (ethanol) concentrations have significant seasonal trends (Figure 4.9). As mentioned previously, the striking contrast in the C_3H_6 (propene) / C_2H_5OH (ethanol) ratio between winter and summer has not been observed previously. This variation is currently unexplained. It may be due to an unannounced addition of C_2H_5OH (ethanol) to fuel by the gasoline suppliers or alternatively due to unexplained photochemistry. This striking contrast between winter and summer requires further research.

To improve petrol quality, fuel additives have been used; methyl tertiary butyl ether (MTBE) to substitute for lead compounds, oxygenates to reduce the amount of high-octane aromatic HCs. These common oxygenates that make oxygen more abundant in the combustion reactions include CH_3OH (methanol), C_2H_5OH (ethanol), and other ethers and alcohols. In addition to the emissions from combustion from the vehicles, these alcohols increase the evaporative emissions from the petrol. It has been reported about 30- 50 % of total HC emissions are in vehicle evaporative emissions [Colls, 2002]. As noted earlier, the higher summer results for C_2H_5OH (ethanol) are not known at present. It should be noted however, that higher temperatures can cause high levels of C_2H_5OH (ethanol) through evaporation.

Furthermore, Christchurch likes many other cities has numerous hotels and restaurants that sell alcoholic beverages. This is also a large brewery for beer in the city centre operating 24 hours a day. C_2H_5OH (ethanol) is also a fermentation product that could be produced from rotting fruit and plants and composting of vegetable matter. These would all be alternative sources of C_2H_5OH (ethanol) emissions in addition to transport.
It should be remarked for C_2H_4 (ethylene) levels, that the gas plays a major role in plant growth and development (Chapter 1). Further, plants under stress can produce C_2H_4 (ethylene) at dramatically higher (up to 400 fold) production rates than normal. Example of stress - induced C_2H_4 (ethylene) production occurs when plants are exposed to atmospheric pollutants viz O_3 (ozone), PAN (peroxyacetyl nitrates) and SO_2 (sulphur dioxide). [Wayne, 2000]

The levels of aromatic C_6H_6 (benzene) were found to be quite high in this study. Several years ago it was recorded that Riccarton had very high concentration of this pollutant (20.1, 18.6 $\mu g/m^3$) in ambient air [Campbell, 1998, Chiodo et al, 2000].

In Western European and North American cities, at the kerbside of busy streets, C_6H_6 (benzene) was measured at level of 30 $\mu g/m^3$ [Hester and Harrison, 1998]. They also noted that C_6H_6 (benzene) concentrations were two times higher in winter than in summer ambient air. The result reported here show levels of benzene that are substantially higher during the peak periods.

The results show that concentrations of C_3H_6 (propene) increase during the night time especially during the winter season. The results also show that the difference in concentrations of the two dominant VOCs, C_3H_6 (propene) and C_2H_5OH (ethanol), is greatest during winter nights.

It is not obvious why the observed VOCs; C_2H_5OH (ethanol), C_3H_6 (propene), CH_3CHO (acetaldehyde), NH_3 (ammonia), C_6H_6 (benzene), C_2H_4 (ethylene), CH_3OH (methanol), C_7H_8 (toluene), and C_8H_{10} (xylene), exhibited a seasonal relationship. Nevertheless, the observed data seems to suggest that emissions from motor vehicles and photochemical reactions most strongly influence the concentrations of VOCs in ambient air of Christchurch during summer, and the emissions from home heating appliances account for the winter concentrations.

Mohamed (2002) noted that 'the atmosphere is an open system, and concentrations of any elements are not only dependent on the emission strength and chemical/photochemical process, they depend on meteorological condition such as atmosphere stability, wind velocity, and direction as well.' As mentioned in Chapter 2 that while the sample were being taken the local meteorological conditions data were also recorded. For this study, it is clear that wind direction and speed contribute to the creation of a microenvironment.

4.4.1 Recommendations

1) Research limitations of this study

- Only six air samples were taken from each site during each season.
- More accurate data could be obtained by using the MUI mode of operation of the SIFT-MS instrument.

2) Future

- The most striking finding was that the seasonal C_3H_6 (propene) /C_2H_5OH (ethanol) ratio is not one and this needs to be investigated further.
- It is recommended that the air monitoring should be conducted during the long summer holiday period with larger numbers of samples.
- It is recommended that many more breath samples are analyzed from the different sites.
- It is recommended that the smaller mobile SIFT-MS instruments are taken to individual sites for in situ observations, thereby omitting the role of balloons as sample containers.
- The study needs to be extended over several seasons to examine the reproducibility of the seasonal variations uncovered here.

Chapter 5 Smokers

5.1 Background

As people in air polluted areas have potential health risks similar to those of smokers it is therefore interesting to compare breath samples from smokers and non-smokers.

Previous studies [US.EPA, 2002, WHO, 2002, Fowles et al, 2000] identified that at least 43 distinct cancer-causing chemicals are present in tobacco smoke viz C_4H_6 (1,3 - butadiene), CH_3CHO (acetaldehyde) and (C_6H_6) benzene. Smoking is also directly responsible for 87 percent of lung cancer cases and causes most cases of emphysema and chronic bronchitis. Smoking, a major factor in coronary heart disease and strokes may be causally related to malignancies in other parts of the body; and has been linked to a variety of other conditions and disorders, including slowed healing of wounds, infertility, and peptic ulcer disease.

The effect of smoking on pregnant women is clear. Twenty to thirty percent have low-birth weight babies, up to 14 percent have preterm deliveries, and some 10 percent of all infant deaths occur to mothers who smoke. Even apparently healthy, full-term babies of smokers have been found to be born with narrowed airways and curtailed lung function. Smoking by parents is also associated with a wide range of adverse effects in their children, including exacerbation of asthma, increased frequency of colds and ear infections, and sudden infant death syndrome. In the USA, it is estimated that 150,000 to 300,000 cases of lower respiratory tract infections in children less than 18 months of age, resulting in 7,500 to 15,000 annual hospitalizations, are caused by second hand smoke.

Also in the USA, smoking-related diseases claim an estimated 440,000 lives each year, including those affected indirectly, such as babies born prematurely due to prenatal maternal smoking and some of the victims of "second hand" exposure to tobacco's carcinogens. Smoking costs the United States approximately $150 billion each year in health-care costs and lost productivity. [Fowles and Bates, 2000]

5.2 Method

Previous researchers have focused mainly on the components of cigarette smoke emission or gas evaporated from tobacco before it is burnt. This previous research was mainly directed at identification of potentially dangerous VOCs from tobacco rather than identifying how much of the VOCs remain in the individual. In this study we look for the presence of VOCs in breath samples from smokers. It is known that some VOCs can be adsorbed in blood and exhaled in breath e.g. C_2H_5OH (ethanol). The aim of this study was to compare the difference in concentration of the selected VOCs in exhalations from smokers, and non smokers and to examine the breath of people exposed to polluted air.

In the detection and analysis of trace components in air, large sample volumes are required whereas this is not possible for breath analysis without going to complicated collection methods. By using the SIFT-MS technique these experimental difficulties are removed.

The experiment was carried out as follows;

- Breath analyses of some selected volatile organic compounds of 15 smokers and 16 non-smokers were carried out using SIFT-MS. The expired breath from the subjects were analysed by both directly blowing into the SIFT-MS instrument and using balloon sampling. The smokers and non-smokers participating in the study were healthy subjects. The smokers had all smoked for at least 4 years, and the non –smoker volunteers were not exposed to passive smoking.
- The balloon samples were collected in 6 litre Mylar bags from Betallic LLC, USA, stored at room temperature and then analysed by injection into the SIFT - MS instrument.
- Each subject provided information on age, gender, occupation, health condition, education and also nationality as shown in Table 5.1. All subjects were in normal good health so this information is not shown.
- Twenty-one volunteers out of the total are international students living within Christchurch city.

Table 5.1 Overview information of subjects

Group	Subgroup	smokers	Non –smokers	Total
Gender	Male	11	7	18
	Female	4	9	13
Education	Bachelor	5	6	11
	Master	6	7	13
	PhD	1	3	4
	Other	3		3
Country	New Zealand	7	3	9
	USA	0	4	4
	Thailand	1	3	4
	China	2	1	3
	Germany	2	1	3
	Vietnam	0	2	2

Group	Subgroup	smokers	Non –smokers	Total
	Indonesia	1	0	1
	Japan	1	0	1
	Korea	1	0	1
	Peru	0	1	1
	Malaysia	0	1	1
	Serbia Monte Negro	0	1	1
Occupation	Student	11	16	27
	Non Student	4	0	4
Age	Range	22-53	19- 36	19 - 53
	Average	31	27	29

5.3 Experimental results

As mentioned in Chapter 3 that there are two different modes of operation in SIFT –MS; The full mass scan mode and the multi ion selected mode. The breath samples were analysed using the first mode of operation to examine the extent of VOCs present in exhalations from the groups of people as described in Table 5.1.

5.3.1 Results from Mass Scan mode

Examples of mass scan spectra, from breath sampling analysis shows the mass scan of smokers (Figures 5.1), non smokers (Figures 5.2) and subjects exposed to polluted air (Figure 5.3). In Figure 5.3c subject provided the expired breath following a brief exposure to polluted air during a period of high pollution.

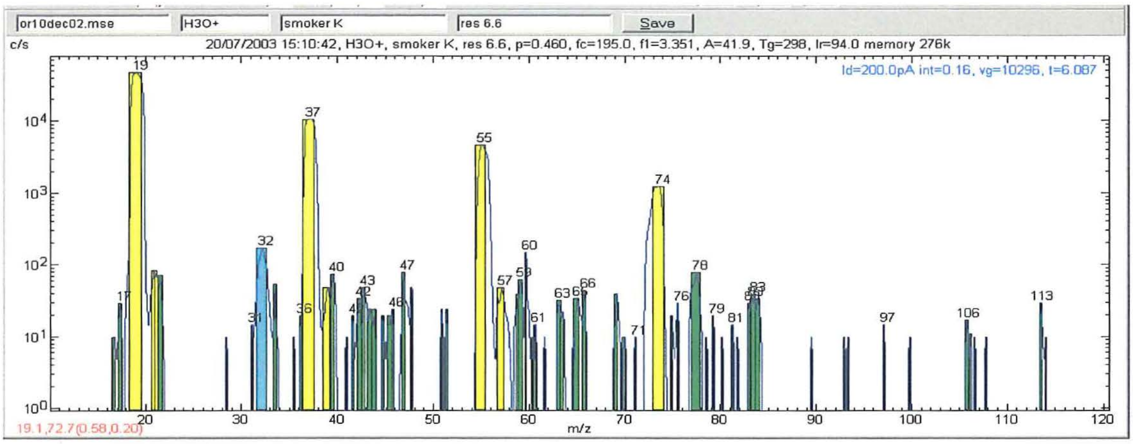


Figure 5.1 Breath profile from smoker

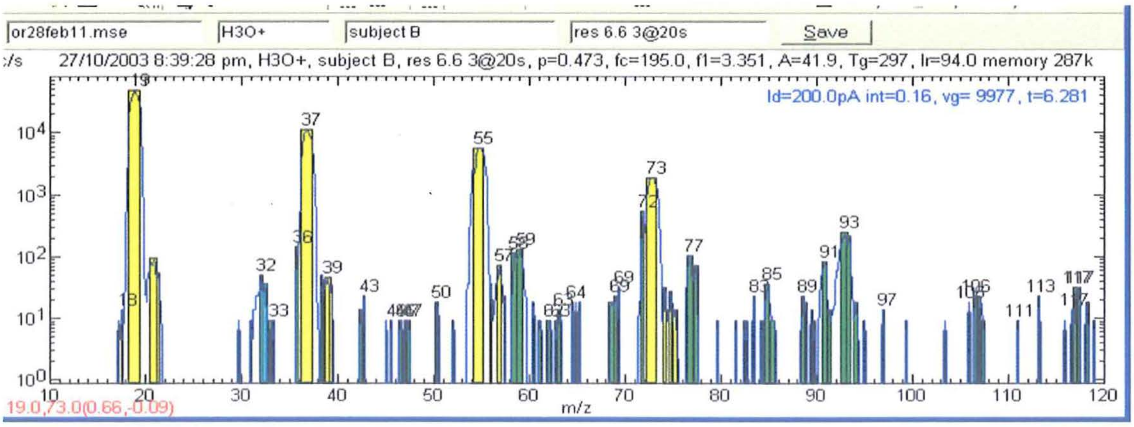


Figure 5.2 Breath profile from non-smoker

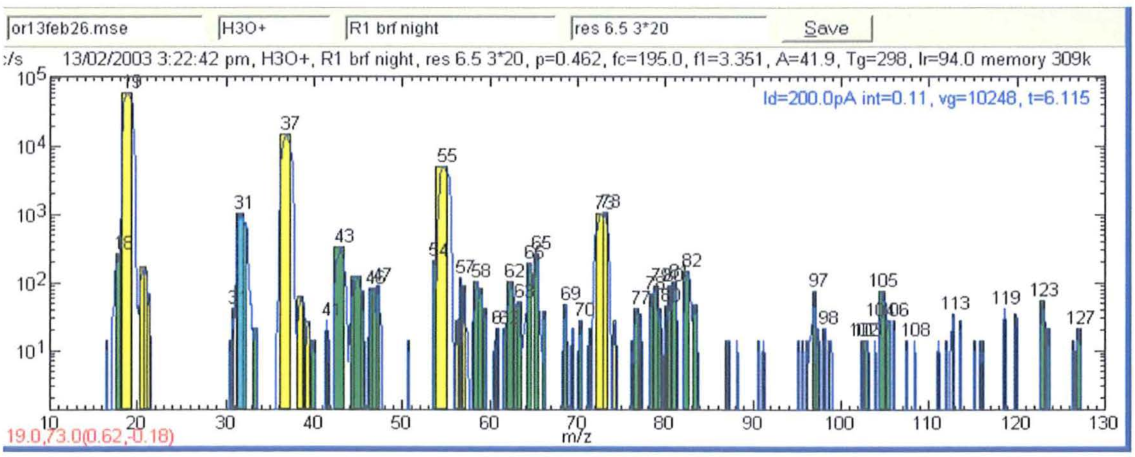


Figure 5.3 Breath profile from an individual subject briefly exposed to high ambient air city VOCs

From these mass spectra the selected compounds that were found in the breath were then analysed and compared. It is important to note that the analytes in breath shown in this chapter may be over estimated in the absolute results is in order as we now realise that higher clusters of water need to be included in the analyses

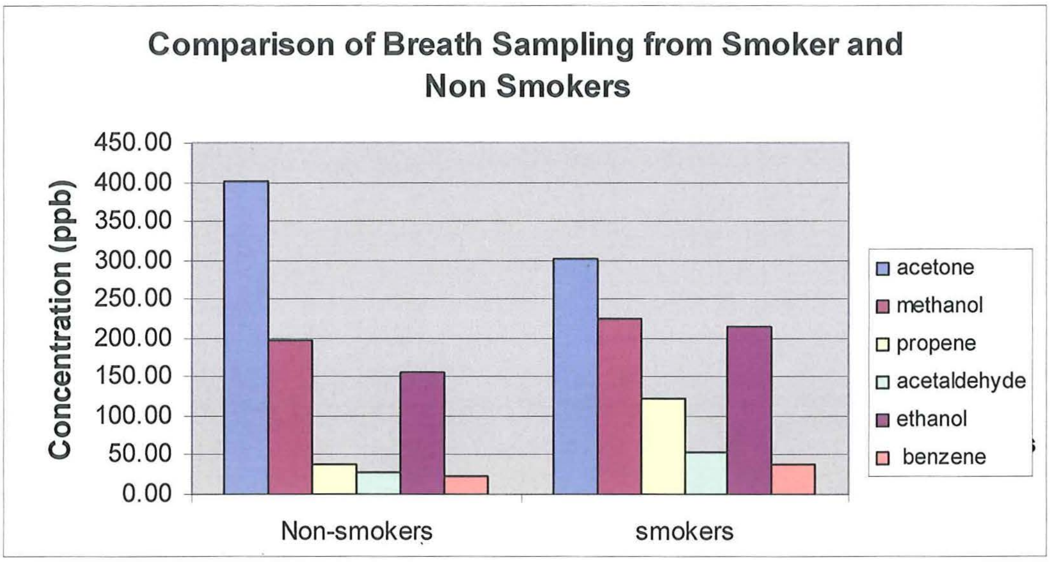


Figure 5.4 Distribution of VOCS in smokers and non-smokers breath.

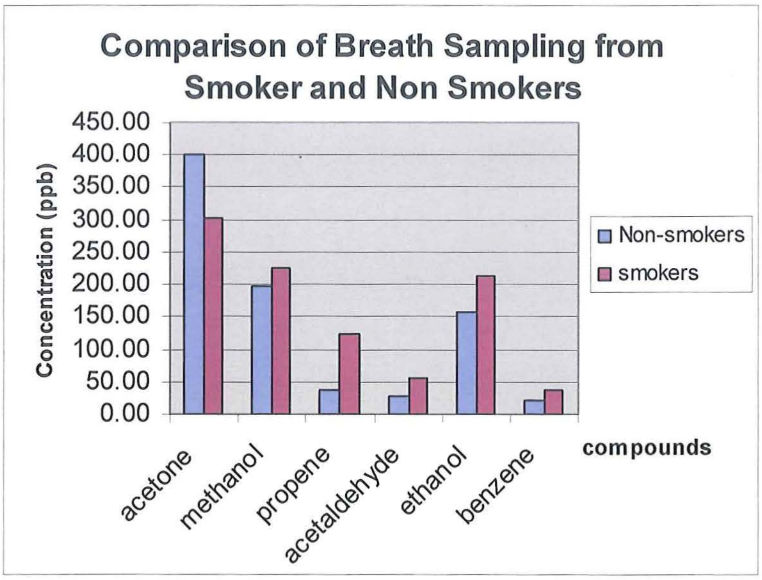


Figure 5.5 Comparison of VOCs; acetone, methanol, propene, acetaldehyde, ethanol and benzene[a] between smokers and non smokers breath.

[a] Footnote. The results shown here and elsewhere in this study for benzene using H_3O^+ as the precursor ion overestimate the amount of benzene in the sample. Throughout this project, benzene was monitored by its product signal at m/z=79. Work completed after these measurements were made has since shown that benzene is accurately monitored using the NO^+ and O_2^+ precursor ions. The results of benzene concentrations from H_3O^+ also include contributions to the m/z=79 peak from water clusters of acetic acid and CH_3CO^+. They therefore overestimate the amount of benzene in the sample

The comparison of selected compounds between smokers and non-smokers show some differences. The dominant VOC in all subjects is C_3H_6O (acetone) and this is at lower concentrations in smokers' breath. The other VOCs such as CH_3OH (methanol), C_2H_5OH (ethanol), C_3H_6 (propene), C_2H_4O (acetaldehyde), and C_6H_6 (benzene) show slight to significant increases in the smoker group over the non-smoker population.

Data was only available from one subject who was exposed to a high pollution episode with in the city. This data is not statistically significant in that it came from a single individual but nevertheless it makes an interesting comparison with the smoker and non- smoker population. This comparison is shown in Figure 5.6

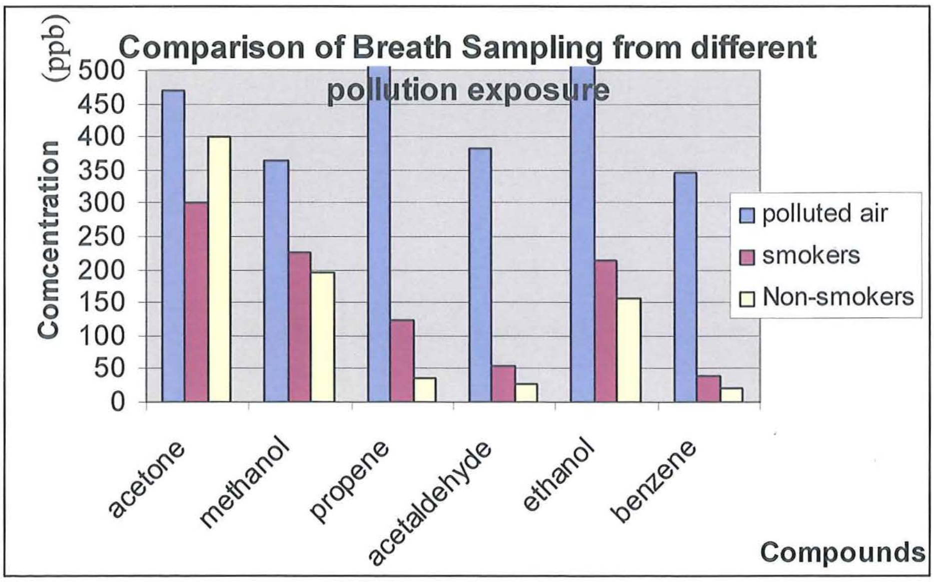


Figure 5.6 Comparison of breath samplings from groups of individuals exposed to the different types of pollution

It is interesting to note that C_3H_6O (acetone) concentration increases after a short exposure to high air pollution which is similar to the results of a previous study of breath volatiles in cigarette smokers after 10 minutes of smoking. [Senthilmohan et al, 2002].

However, since the concentration of C_3H_6O (acetone) is lower in smokers' breath it could be that the body reacts to cigarette pollution differently according to the time of exposure.

It could be argued that the concentration of C_3H_6O (acetone) in smokers breath might be lower because the smokers are more adapted to a polluted environment and thereby the body produces less C_3H_6O (acetone). Whereas the concentration of C_3H_6O (acetone) in a non-smoker's breath exposed to the polluted environment for a shorter time might be higher because the body produces more C_3H_6O (acetone) when exposed to the polluted environment.

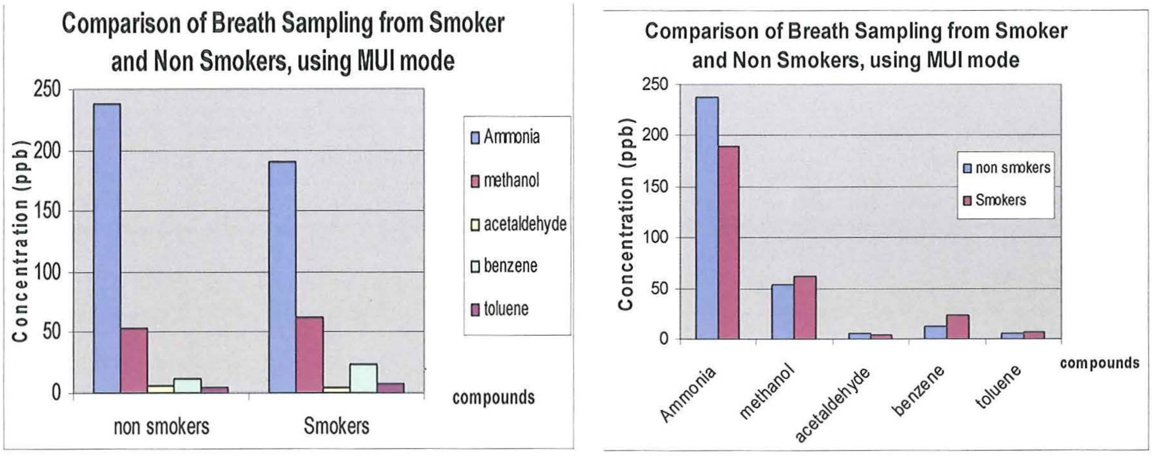
People respond in different ways to exposure to pollutants and their responses can influence the biomechanism [Kingham, 2003]. In opposition to these suggestions research from Euler et al [1996] showed there was little difference in concentration of C_3H_6O (acetone) in the breath samples of smokers and non-smokers.

The results shown here from examining smoker's breath and also in Chapter 4 from breath exhalation in a polluted environment demonstrate a tendency for certain VOCs to accumulate in the human body and to concentrate in the exhaled breath. There is some promise that studies of this type may be used to identify specific VOC residues within the body after exposure to polluted environments.

5.3.2 Results from multi selected ion mode

Samples were obtained from more than 10 smokers and 10 non-smokers and analyzed using the multi selected ion mode (MUI) of operation. These average results are shown in Figures 5.7 (a) and (b).

The multi selected ion mode (MUI) can only be used in the lab so it was not possible to get the data in real time from the sampling site after a short exposure to urban air pollution.



(a) (b)

Figure 5.7 Comparison of breath samplings from smokers and non smokers by compounds distribution (a) and by group of subjects (b).

5.4 Discussion and conclusion

It is interesting to look at the comparison between the three groups of subjects as described.

<u>Group A:</u> represents one subject exposed to urban ambient air from 20 to 120 minutes. This means the subject was exposed to relatively high levels of air pollutants for a short period of time.

<u>Group B</u>: 15 subjects in all who were healthy smokers and therefore considered to have exposure to low levels of air pollutants over a long term.

Group C: 16 subjects in all who were healthy non-smokers, who were rarely exposed to air pollutants.

The trends for each compound among the three groups are quite noticeable. In Figure 5.6, the C_3H_6O (acetone) level is reduced in the smokers group (Group B) but increased in the samples from Group A. It is noted that CH_3OH (methanol), C_2H_5OH (ethanol), C_3H_6 (propene), C_2H_4O (acetaldehyde), and C_6H_6 (benzene) all appear at the higher levels in breath samples taken from Group A.

According to this analysis of exposure to air pollution for people in Christchurch, it is noted that the daily average pollutant concentrations in the metropolitan area probably cause no significant problems for the great majority of population. In the pollution episode situations, however, there may be an increase in symptoms suffered by members of sensitive population groups (those with bronchial and heart disorders, children and old people) [Helsinki Metropolitan Area Council, 2003]. There are considerable differences in individual sensitivity within these population groups. The frost which accompanies pollution episodes in winter may increase the symptoms caused by pollutants, especially in the case of asthmatics. In the long run, pollutants may also have an impact on the occurrence of some bronchial disorders.

Further work in body chemistry should be conducted to see how the body adsorbs and copes with these chemicals and the effects of exposure to the low concentration in the long term.

5.4.1 Limitation of this study

Most of subjects were students between the age of 20-35. A more balanced representation to get more varieties in the population would have been better. Also the group sizes were too small for statistical analysis. However, this study can be considered as a pilot for planning future trials.

5.4.2 Recommendation for future work.

The comparative study with smokers and non-smokers needs to be repeated using the MUI mode of SIFT-MS operation. Differences between the two groups are too small and the more accurate data provided by MUI operation is required. The work described in this subject is merely a pilot study for a more serious investigation using a much larger sample size.

Chapter 6 Conclusion

6.1 Conclusion

It was stated in the UK National Air Quality Strategy that for air quality monitoring "the objective should apply to non-occupational, near ground level outdoor locations where a person might reasonably be expected to be exposed over the relevant averaging period" [Hester and Harrison, 1998]. The samples of ambient air described in this thesis were obtained at a height of 1.7 ± 0.2 meter that approximated breathing height.

Taking on board the comments of the UK National Air Quality Strategy, the present study monitors the very low amounts of volatile organic compounds in the Christchurch atmosphere viz ,NH_3 (ammonia), C_2H_4 (acetylene), C_3H_6 (propene), CH_3OH (methanol), C_2H_5OH (ethanol), CH_3CHO (acetaldehyde), C_6H_6 (benzene), C_7H_8 (toluene) and C_8H_{10} (xylene).

The examination of these compounds was achieved by sampling the ambient air around the city at three selected sites during the winter of 2002. The number of sites was then expanded to nine, covering more urban areas in the summer of 2002 - 2003. In earlier investigations, the data was collected at a standard height of 3 meters above ground level [Ecan, 2002]. In this study, the samples were taken at a breathing height, 1.5 to 2 meter, since concentration of these air pollutants at this level is most likely to affect human health.

Little data was available of VOCs in Christchurch air prior to this study due to the limitations of analytical methods available. SIFT-MS (Selected Ion Flow Tube Mass Spectrometry) is an ideal technique for examining VOC concentrations ranging from 10 ppb to 40 ppm. The availability of this technique thus enhances research in atmospheric chemistry and environmental monitoring opening up new possibilities for real time monitoring. The presence of the SIFT-MS instrument at the University of Canterbury has enhanced research in atmospheric chemistry and environmental monitoring for the Christchurch region.

At unexpected outcome of this study was the seasonal variation observed for some VOCs. There appears to be a distinct difference between winter and summer levels of C_3H_6 (propene) and C_2H_5OH (ethanol). These two VOCs exhibit an inverse relationship. In winter, the C_3H_6 (propene) concentration is highest but it is lower than C_2H_5OH (ethanol) in the summer samples. No definitive cause for this variation was established. There are several explanations for these trends. Possibilities include more C_2H_5OH (ethanol) vaporization during the summer due to higher temperatures, elevated decomposition of organic waste in the summer, and increased photochemistry during the summer. It is worth noting that New Zealand experiences a marked increase in UV intensity in summer as a result of the Antarctic ozone hole formation during the spring warming in the months September to January.

The research shows the presence of C_6H_6 (benzene) at higher levels compared to C_7H_8 (toluene). This result is opposite to what is observed in cities in other countries. One possible reason for C_6H_6 (benzene) at enhanced levels compare to northern hemisphere cities might be the reaction of C_7H_8 (toluene) with hydroxyl radicals (OH) [Wayne, 2000]. It should also be noted that higher C_6H_6 (benzene) concentration can simply be the result of higher percentages of aromatics in New Zealand petrol [The New Zealand Refining Company Ltd, 1997].

6.2 Recommendations

6.2.1 In terms of management

- Local Administration;

  At the present time there are several incentives to promote pollution abatement in the Christchurch area. However, in the drive to lower pollution, certain events can have a confounding effect on the pollution levels. For example, there is an incentive towards greater use of electrical heating. Nevertheless, low lake levels in the winter of 2003 negated the move to electrical heating resulting in a substantial rise in the price of electricity. Economic factors clearly need to be factored into the pollution equation.

  "Push and pull" "win- win solution" strategies should be applied with stronger penalties for those failing to meet the norms, and drawing defaulters to the attention of the public.

- Education of Individuals;

  The public needs to be instructed in understanding what appropriate alternative fuels are available. These alternative fuels must be affordable in comparison to the less polluting energy sources.

- Research Institutes;

A substantial amount of scientific research on aspects of pollution has been or is in progress and there is a body of data available. But even though considerable research is being done, the success of any program to reduce pollution depends on the ability to translate the findings of the research into the lifestyle of the citizens. Probably much of the research still does not take into account the perception of local people and financial constraints.

- The public awareness program which ECan conducted by TV, radio, press and web site very intensively during the winter time has highlighted the elevated levels of pollution mainly from particulate matter (PM_{10}). Again, making people aware of a problem is only one part of the equation. An effective strategy goes beyond awareness and will result in behavioural change.

6.2.2 Future Research

- The most striking finding of this study was the seasonal variations in the C_3H_6 (propene) /C_2H_5OH (ethanol) ratio and this is worthy of further investigation.
- It is recommended that the air monitoring should be conducted during the long summer holiday period with larger numbers of samples.
- It is recommended that many more breath samples are analyzed from the different sites to clarify the body reservoirs of the various pollutants.
- It is recommended that the residence time of these pollutants in the body be examined by time variation studies.

- It is recommended that the smaller mobile SIFT-MS instruments be taken to individual sites for in situ measurements, thereby eliminating use of balloons as sample containers.
- The study needs to be extended over several seasons to examine the pattern of the observed seasonal variations.
- This work can be extended to increase the numbers of compounds examined and to consider the effect of the compounds on the body. The results of this work can then be used as the initial database for further research such as biomechanisms for absorption and accumulation of certain species in the body.

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Ten minute average data from St Albans 3 (Coles Pl) ambient air quality monitoring site

	Wind speed at St Albans 3 WS m/s	Wind dir at St Albans 3 WD deg	Ext Temp @ 1m at St Albans 3 Ext T deg C	RH at St Albans 3 RH %	NOx at St Albans 3 NOx ppb	SO2 at St Albans 3 SO2 ugm-3	External Temp @ 10 m at St Albans 3 Ext T @10m deg C
3/07/2002 00:00	0	0	-1.2	98	193	19.9	0.7
3/07/2002 00:10	0	239	-1.4	99	197	19.3	1
3/07/2002 00:20	0	0	-1.1	99	182	17.2	1.3
3/07/2002 00:30	0	0	-1.2	98	170	16	1
3/07/2002 00:40	0	0	-1.5	99	168	14.9	1.1
3/07/2002 00:50	0	0	-1.5	98	174	15.4	0.9
3/07/2002 01:00	0	0	-1.8	99		15.2	0.7
3/07/2002 01:10	0	0	-1.8	99		15.7	0.6
3/07/2002 01:20	0	0	-1.7	99		15.4	0.2
3/07/2002 01:30	0	0	-1.7	100		15.2	0.2
3/07/2002 01:40	0	0	-1.9	100		15.1	0.2
3/07/2002 01:50	0	0	-2.2	100	152	14	-0.1
3/07/2002 02:00	0	0	-2.3	100	143	13.2	-0.2
3/07/2002 02:10	0	304	-2	100	134	12.6	-0.2
3/07/2002 02:20	0.9	307	-2	101	119	12.2	-0.2
3/07/2002 02:30	0.6	304	-1.9	101	100	11	-0.2
3/07/2002 02:40	0	0	-2	101	95	11.1	-0.4
3/07/2002 02:50	0	292	-2	101	91	10.6	-0.3
3/07/2002 03:00	0.5	283	-2.1	101	90	10.6	-0.3
3/07/2002 03:10	1.3	298	-1.9	101	82	9.1	-0.1
3/07/2002 03:20	0.3	303	-1.6	101	79	9	-0.2
3/07/2002 03:30	0.1	190	-1.5	101	76	8.2	-0.3
3/07/2002 03:40	0.7	183	-1.2	101	69	7.6	0
3/07/2002 03:50	0	0	-1.1	101	56	7.4	0.4
3/07/2002 04:00	0	0	-1	101	54	6.3	0.6
3/07/2002 04:10	0	250	-0.9	101	53		0.6
3/07/2002 04:20	0.1	254	-0.7	100	48		0.7
3/07/2002 04:30	0.5	267	-0.6	100	44		0.8
3/07/2002 04:40	0.8	256	-0.4	100	44		0.9
3/07/2002 04:50	0.7	252	-0.3	99	48	5.4	1
3/07/2002 05:00	0	0	-0.2	99	49	5.7	1.1
3/07/2002 05:10	0.9	260	-0.1	99	47	6.2	1.3
3/07/2002 05:20	0.1	256	0	98	48	7.1	1.6
3/07/2002 05:30	0	0	0	98	49	7.7	1.6
3/07/2002 05:40	0	0	-0.2	97	48	7.3	1.6
3/07/2002 05:50	0.6	282	-0.2	97	51	8	1.3
3/07/2002 06:00	1.7	273	-0.4	98	46	8.1	1.2
3/07/2002 06:10	1.3	298	-0.6	98	44	7.7	1
3/07/2002 06:20	0.1	297	-1	98	40	6.3	0.7
3/07/2002 06:30	0.2	296	-1.2	99	37	6.3	0.5
3/07/2002 06:40	1.2	293	-1.5	99	34	5.5	0.5
3/07/2002 06:50	0.2	272	-1.8	99	41	6	0.4
3/07/2002 07:00	1	257	-2	99	44	5.6	0.5
3/07/2002 07:10	2	264	-1.9	99	48	7	0.6
3/07/2002 07:20	2	250	-1.9	98	62	8.1	1.3
3/07/2002 07:30	1.5	273	-1.9	95	76	11	1.7
3/07/2002 07:40	1.4	289	-1.8	95	89	12	1.1
3/07/2002 07:50	1.5	293	-2	96	114	13.3	0.6
3/07/2002 08:00	1.4	288	-2.1	97	145	16	0.3
3/07/2002 08:10	1	291	-2.1	98	187	17.3	0.3
3/07/2002 08:20	0.2	275	-2.2	98	240	20.7	0.4
3/07/2002 08:30	0.5	293	-2	98	211	20.8	0.6
3/07/2002 08:40	0	0	-2	98	273	23.2	0.6
3/07/2002 08:50	0	0	-2	98	317	26.6	0.5
3/07/2002 09:00	0.9	258	-2	98	347	27.5	0.8
3/07/2002 09:10	1.8	254	-1.7	97	343	28.1	1.2
3/07/2002 09:20	1.7	254	-0.2	94	339	30.2	2.4

Ten minute average data from St Albans 3 (Coles Pl) ambient air quality monitoring site

	Wind speed at St Albans 3 WS m/s	Wind dir at St Albans 3 WD deg	Ext Temp @ 1m at St Albans 3 Ext T deg C	RH at St Albans 3 RH %	NOx at St Albans 3 NOx ppb	SO2 at St Albans 3 SO2 ugm-3	External Temp @ 10 m at St Albans 3 Ext T @10m deg C
3/07/2002 09:30	0.9	256	1.3	89	279	31.2	3.4
3/07/2002 09:40	1.1	261	2.5	86	305	32.9	4.2
3/07/2002 09:50	0.3	240	4.5	80	222	33	5.7
3/07/2002 10:00	0.4	247	5.9	74	146	28.6	6.4
3/07/2002 10:10	1.1	244	6.3	73	92	23.9	6.6
3/07/2002 10:20	1.2	250	6.1	71	76	24.1	6.5
3/07/2002 10:30	0.4	280	6	71	97	25.2	6.6
3/07/2002 10:40	0.5	288	7	70	158	29.6	7.2
3/07/2002 10:50	0.3	287	7.6	69		28	7.5
3/07/2002 11:00	0.3	262	7.9	67		16.2	8.5
3/07/2002 11:10	0.3	278	8.8	65		14.5	9
3/07/2002 11:20	0.2	263	9.5	62		14.6	9.9
3/07/2002 11:30	0.2	255	9.9	59		14.1	10.7
3/07/2002 11:40	0.7	231	10.4	59		14.1	10.8
3/07/2002 11:50	0.5	243	11.1	58		13.6	11.1
3/07/2002 12:00	0.2	260	11.7	57		14.5	11.4
3/07/2002 12:10	0	156	11.8	55		15.2	12.2
3/07/2002 12:20	0.3	233	12.4	51		14.9	12.8
3/07/2002 12:30	1	227	12.9	49		13.7	13
3/07/2002 12:40	1	240	13.5	49		14.4	13.1
3/07/2002 12:50	1.4	261	13.8	49		12.6	12.7
3/07/2002 13:00	0.7	267	13.6	48	99	11.3	13.3
3/07/2002 13:10	1.2	266	13.6	47	127	11.8	13.5
3/07/2002 13:20	1.3	221	13.7	46	26	10.5	13.4
3/07/2002 13:30	1.1	250	13.9	44	23	10.4	13.4
3/07/2002 13:40	1	238	13.8	42	24	10.3	13.7
3/07/2002 13:50	1.6	244	14.1	41	22	11	14
3/07/2002 14:00	1.6	268	14.2	39	15	7.7	13.8
3/07/2002 14:10	2.4	276	14.3	35	7	3.3	13.4
3/07/2002 14:20	2	273	14.3	35	5	2.1	13.5
3/07/2002 14:30	1.6	284	14.4	34	5	2.3	13.6
3/07/2002 14:40	2	274	14.4	34	5	3.1	13.6
3/07/2002 14:50	1.7	256	14.3	34	7	3.8	13.7
3/07/2002 15:00	1.7	256	14.2	34	7	3.8	13.9
3/07/2002 15:10	1.1	275	14.2	34	7	2.9	13.9
3/07/2002 15:20	0.9	291	13.9	34	7	2.8	13.8
3/07/2002 15:30	1	289	13.5	34	6	3.6	13.9
3/07/2002 15:40	0.9	309	12.8	34	6	3.6	13.8
3/07/2002 15:50	0.8	331	11.7	34	7	3	13.8
3/07/2002 16:00	0.6	324	11.2	34	6	2.6	13.6
3/07/2002 16:10	1	309	10.8	35	13	3.8	13.6
3/07/2002 16:20	1.4	352	10.5	40	14	4	13.2
3/07/2002 16:30	1.8	26	9.9	57	22	7.2	11.9
3/07/2002 16:40	1.8	27	9.2	60	26	8.1	11.1
3/07/2002 16:50	1.4	34	8.6	62	32	9.5	10.5
3/07/2002 17:00	1	39	7.7	66	50	14.5	10.1
3/07/2002 17:10	1.3	63	6.7	69	108	18.2	9.6
3/07/2002 17:20	0.2	81	6	70	104	18.6	9.2
3/07/2002 17:30	1.2	110	5.4	72	158	19.5	8.8
3/07/2002 17:40	1.4	107	5.1	75	201	25.1	8.4
3/07/2002 17:50	1.6	109	5	78	241	29	8.3
3/07/2002 18:00	1	89	5	80	170	26.5	8.1
3/07/2002 18:10	1.4	84	4.4	82	179	22	8
3/07/2002 18:20	1.2	95	3.8	83	212	22	7.9
3/07/2002 18:30	0.6	99	3.2	85	231	23.8	7.6
3/07/2002 18:40	0	0	2.8	85	205	19.4	7.4
3/07/2002 18:50	0	0	2.6	86	185	17.7	7.2

Ten minute average data from St Albans 3 (Coles Pl) ambient air quality monitoring site

	Wind speed at St Albans 3 WS m/s	Wind dir at St Albans 3 WD deg	Ext Temp @ 1m at St Albans 3 Ext T deg C	RH at St Albans 3 RH %	NOx at St Albans 3 NOx ppb	SO2 at St Albans 3 SO2 ugm-3	External Temp @ 10 m at St Albans 3 Ext T @10m deg C
3/07/2002 19:00	0	88	2.3	87	234	20.1	6.7
3/07/2002 19:10	0.1	87	2.1	88	257	23.3	6.7
3/07/2002 19:20	0	0	1.9	89	265	22.4	6.4
3/07/2002 19:30	0	0	1.5	90	281	24.1	6.3
3/07/2002 19:40	0	0	1.2	91	280	23.6	6.3
3/07/2002 19:50	0	0	0.9	91	297	22.3	6.1
3/07/2002 20:00	0	0	1	92	363	26.1	6.1
3/07/2002 20:10	0	0	0.8	92	394	28.6	6.1
3/07/2002 20:20	0	0	0.6	90	410	30.1	6.1
3/07/2002 20:30	0.6	91	0.7	87	375	27.8	6.1
3/07/2002 20:40	0.8	91	0.6	84	368	28.8	5.9
3/07/2002 20:50	0.1	90	0.5	85	325	28.7	5.6
3/07/2002 21:00	0	90	0.4	87	290	25.5	5.4
3/07/2002 21:10	0	0	0.2	89	315	24.4	5.1
3/07/2002 21:20	0	0	-0.1	91	351	25.7	5
3/07/2002 21:30	0	0	-0.1	94	355	26	4.8
3/07/2002 21:40	0	0	-0.2	96	348	25.4	4.6
3/07/2002 21:50	0	0	-0.2	97	348	25.4	4.3
3/07/2002 22:00	0	86	-0.4	97	355	25	4.1
3/07/2002 22:10	0	0	-0.4	99	354	25.7	4.4
3/07/2002 22:20	0.6	339	-0.4	99	321	24.9	4.3
3/07/2002 22:30	0	339	-0.3	99	332	24.3	3.8
3/07/2002 22:40	0	0	-0.4	100	337	23.1	3.2
3/07/2002 22:50	0	0	-0.4	100	329	22.5	2.9
3/07/2002 23:00	0	0	-0.6	101	332	23.5	3
3/07/2002 23:10	0	0	-0.6	101	317	22.4	3
3/07/2002 23:20	0	0	-0.9	101	316	21.8	3
3/07/2002 23:30	0	0	-0.9	102	302	22.2	3.3
3/07/2002 23:40	0	0	-0.8	101	296	22.4	3
3/07/2002 23:50	0	0	-0.8	102	289	21.6	2.9
4/07/2002 00:00	0	0	-1	102	280	21.4	2.7
9/07/2002 12:00	2.1	203	11.1	75	14	10.9	10.4
9/07/2002 12:10	2.2	204	11.1	73	13	10.4	10.6
9/07/2002 12:20	3	220	11.5	72	12	9.8	10.8
9/07/2002 12:30	2.3	207	11.4	72	10	7.3	10.8
9/07/2002 12:40	2.6	199	11.2	71	8	6.5	10.9
9/07/2002 12:50	2.3	192	10.9	72	8	5.6	10.9
9/07/2002 13:00	3.3	184	10.6	72	7	4.7	10.6
9/07/2002 13:10	2.2	186	11	72	6	4.2	10.8
9/07/2002 13:20	3.1	211	11.3	70	8	4.6	10.9
9/07/2002 13:30	2.7	207	11.2	70	7	4	10.8
9/07/2002 13:40	2.8	191	11.2	67	8	2.8	11
9/07/2002 13:50	2.8	184	11	65	6	2.2	11.1
9/07/2002 14:00	2.9	207	11.2	63	5	1.4	11.1
9/07/2002 14:10	2.8	203	11.6	66	6	1.8	11.2
9/07/2002 14:20	2.3	220	11.4	69	5	2.8	11.1
9/07/2002 14:30	3	227	11.9	68	5	3.6	11.4
9/07/2002 14:40	2.8	219	11.7	68	6	3	11.2
9/07/2002 14:50	2.2	215	11.6	69	8	4.1	11.3
9/07/2002 15:00	2.6	210	11.8	68	8	3.7	11.4
9/07/2002 15:10	2.8	230	11.7	68	8	3.7	11.2
9/07/2002 15:20	2.8	221	11.4	70	8	3.7	11.1
9/07/2002 15:30	2.4	217	10.8	68	7	3	11.1
9/07/2002 15:40	2	228	10.7	67	8	2.9	11.2
9/07/2002 15:50	2.3	233	10.2	66	10	2.6	11.3
9/07/2002 16:00	2.2	235	9.7	67	9	2.2	11.2

Appendix B. Geography department weather data

<u>SAMPLE OF RAW DATA</u>

```
et surface_wind
  1 select  agent_no,
  2    substr(to_char(obs_date,'YYYYmmdd:HH24mi'),1,14) "DateTime-UTC  ",
  3    frequency,orig_obs_origin,
  4    direction DIR, round(speed*1.94254) "sfc KTS",
  5    period,
  6    direction_rel DR, speed_rel SR
  7 from surface_wind
  8 where agent_no in ('4843')
  9    and frequency in ('H')
 10    and obs_date between to_date('20020702:0000') and
to_date('20020908:0000')
 11* order by 1,2
SQL> /
 AGENT_NO DateTime-UTC  F O      DIR    sfc KTS     PERIOD D S
 ---------- ------------- - - ---------- ---------- ---------- - -
      4843 20020702:0000 H M      280        4     .1667
      4843 20020702:0100 H M      210        4     .1667
      4843 20020702:0200 H M      210        3     .1667
      4843 20020702:0300 H M      180        6     .1667
      4843 20020702:0400 H M      160        7     .1667
      4843 20020702:0500 H M      180        4     .1667
      4843 20020702:0600 H M      180        2     .1667
      4843 20020702:0700 H M      260        2     .1667
      4843 20020702:0800 H M      270        3     .1667
      4843 20020702:0900 H M      320        2     .1667
      4843 20020702:1000 H M      290        3     .1667
      4843 20020702:1100 H M      300        3     .1667
      4843 20020702:1200 H M        0        0     .1667
      4843 20020702:1300 H M      300        1     .1667
```

4843 20020702:1400 H M	290	1	.1667
4843 20020702:1500 H M	300	3	.1667
4843 20020702:1600 H M	270	3	.1667
4843 20020702:1700 H M	240	2	.1667
4843 20020702:1800 H M	260	1	.1667
4843 20020702:1900 H M	270	1	.1667
4843 20020702:2000 H M	300	2	.1667
4843 20020702:2100 H M	0	0	.1667
4843 20020702:2200 H M	300	2	.1667
4843 20020702:2300 H M	20	2	.1667
4843 20020703:0000 H M	20	1	.1667
4843 20020703:0100 H M	260	4	.1667
4843 20020703:0200 H M	250	3	.1667
4843 20020703:0300 H M	260	2	.1667
4843 20020703:0400 H M	20	1	.1667
4843 20020703:0500 H M	40	5	.1667
4843 20020703:0600 H M	60	4	.1667
4843 20020703:0700 H M	50	2	.1667
4843 20020703:0800 H M	30	1	.1667
4843 20020703:0900 H M	20	2	.1667
4843 20020703:1000 H M	20	2	.1667
4843 20020703:1100 H M	340	1	.1667
4843 20020703:1200 H M	350	2	.1667
4843 20020703:1300 H M	10	2	.1667
4843 20020703:1400 H M	40	3	.1667
4843 20020703:1500 H M	30	3	.1667
4843 20020703:1600 H M	40	2	.1667
4843 20020703:1700 H M	30	4	.1667
4843 20020703:1800 H M	0	0	.1667
4843 20020703:1900 H M	0	0	.1667
4843 20020703:2000 H M	50	1	.1667
4843 20020703:2100 H M	80	2	.1667
4843 20020703:2200 H M	70	4	.1667
4843 20020703:2300 H M	0	0	.1667
4843 20020704:0000 H M	10	5	.1667

Appendix C Kastrell 4000 weather data

Winter Trip	Date	Place	Average		
			Wind speed (m/s)	Temperature(°C)	Relative Humidity (RH)
First Day	2/7/2002	Hornby	0.00	9.00	43.45
		Ricarton	0.00	10.70	43.40
		StAlban	0.00	12.90	43.00
First Night	2/7/2002	Hornby	0.00	2.65	73.95
		Ricarton	0.00	4.50	69.90
		StAlban	0.00	3.93	65.25
Second Night	8/7/2002	Hornby	0.00	7.60	61.15
		Ricarton	0.00	8.95	58.75
		StAlban	0.00	9.30	55.95
Second Day	9/7/2002	Hornby	0.83	5.68	72.43
		Ricarton	0.47	6.03	71.17
		StAlban	0.25	9.40	64.90
Third Day	20/7/2002	Hornby	3.20	16.15	45.25
		Ricarton	0.90	15.45	46.35
		StAlban	4.95	16.55	44.10
Third Night	20/7/2002	Hornby	0.75	11.25	65.85
		Ricarton	0.50	11.80	68.10
		StAlban	2.00	11.10	66.30

Summer Trip	Date	Place	Average		
			Wind speed (m/s)	Temperature(°C)	Relative Humidity (RH %)
First Day	9/12/2002				
		Hornby	2.267	15.033	53.767
		Ricarton	2.433	16.567	50.067
		St.Alban	0.767	19.067	38.800
		R 1Dean	1.933	18.167	42.600
		R 2Clyde	1.233	18.000	38.533
		R3 Columbo	1.000	18.767	37.200
		R4 Worsleys	1.400	23.167	34.367
		R5 Ilam&Ric	2.433	14.767	55.200
		BusEx	0.367	18.333	42.367
First Night	9/12/2002				
		Hornby	0.300	13.400	62.300
		Ricarton	1.000	14.733	59.400
		St.Alban	0.367	14.267	59.167
		R 1Dean	0.233	15.433	53.400
		R 2Clyde	0.167	14.267	61.433
		R3 Columbo	0.567	12.667	64.200
		R4 Worsleys	0.200	13.367	57.767

Summer Trip	Date	Place	Average		
			Wind speed (m/s)	Temperature(°C)	Relative Humidity (RH %)
		R5 Ilam&Ric	0.567	13.667	61.200
		BusEx	0.000	14.733	62.533
Second Day	15/12/2002				
		Hornby	1.133	20.767	16.733
		Ricarton	1.400	19.600	17.933
		St.Alban	0.100	22.133	16.800
		R 1Dean	1.367	23.067	16.133
		R 2Clyde	1.633	19.200	16.000
		R3 Columbo	0.833	19.667	16.300
		R4 Worsleys	0.867	19.000	20.833
		R5 Ilam&Ric	0.400	17.967	23.500
		BusEx	0.200	22.667	16.300
Second Night	15/12/2002	Hornby	1.333	17.133	39.067
		Ricarton	0.533	15.600	48.433
		St.Alban	0.367	16.567	47.067
		R 1Dean	0.767	16.433	49.000
		R 2Clyde	0.300	15.567	54.633
		R3 Columbo	0.700	17.933	42.333
		R4 Worsleys	0.000	14.433	49.933
		R5 Ilam&Ric	0.533	16.333	45.200
		BusEx	0.550	17.100	45.400
Third Day	13/2/2003				
		Hornby	1.133	20.067	59.600
		Ricarton	0.933	18.833	62.400
		St.Alban	2.367	21.333	53.400
		R 1Dean	0.967	22.967	54.367
		R 2Clyde	1.100	20.533	52.967
		R3 Columbo	1.033	19.967	57.533
		R4 Worsleys	2.067	23.000	55.500
		R5 Ilam&Ric	0.833	18.500	65.600
		BusEx	1.367	19.733	58.100
ThirdNight	13/2/2003				
		Hornby	2.333	15.900	65.533
		Ricarton	0.933	15.833	66.033
		St.Alban	1.067	17.633	61.600
		R 1Dean	1.800	16.567	67.500
		R 2Clyde	1.700	15.833	67.667
		R3 Columbo	2.867	17.000	60.133
		R4 Worsleys	1.533	17.067	60.100
		R5 Ilam&Ric	0.467	16.067	61.567
		BusEx	1.567	16.633	64.233

Appendix D Air pollution forecast during winter 2002

WebMail - Christchurch Air pollution forecast - UNCERTAIN

Delete | File | Create | Reply | Reply All | Forward | Previous | Next | Options | Index | Help

Date Sent: Thursday, 15 August 2002 8:04 a.m.

From: Blue Skies Weather <forecasters@blueskies.co.nz> — Add to Address Book

To: "Teresa.Aberkane" <Teresa.Aberkane@ecan.govt.nz>,

Subject: Christchurch Air pollution forecast - UNCERTAIN

Status: Urgent New

AIR POLLUTION POTENTIAL FORECAST

Weather conditions in Christchurch for tonight MAY result in high air pollution.
Please use alternatives to solid fuel burning.

This advice is issued by Blue Skies Weather and Environment Canterbury.

For further information on weather conditions contact Tony Trewinnard, Blue Skies Weather, 03 3264234 or 021 2247767.
For further information on pollution levels contact Teresa Aberkane, Environment Canterbury, 03 3653828..

-- Tony Trewinnard
Blue Skies Weather & Climate Services Ltd
P.O. Box 17621
Christchurch, New Zealand
ph 03 3264234
fax 03 3264235

Secure mode active.

WebMail - Christchurch Air Pollution forecast - LOW

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Date Sent: Sunday, 18 August 2002 8:02 a.m.

From: Blue Skies Weather <forecasters@blueskies.co.nz> | Add to Address Book

To: "Teresa.Aberkane" <Teresa.Aberkane@ecan.govt.nz>,

Subject: Christchurch Air Pollution forecast - LOW

Status: Urgent New

AIR POLLUTION POTENTIAL FORECAST

Weather conditions forecast in Christchurch for tonight ARE UNLIKELY to result in high air pollution.

This advice is issued by Blue Skies Weather and Environment Canterbury.

For further information on weather conditions contact Tony Trewinnard, Blue Skies Weather, 03 3264234 or 021 2247767.
For further information on pollution levels contact Teresa Aberkane, Environment Canterbury, 03 3653828.

-- Tony Trewinnard
Blue Skies Weather & Climate Services Ltd
P.O. Box 17621
Christchurch, New Zealand
ph 03 3264234
fax 03 3264235

Secure mode active.

WebMail - Christchurch Air pollution forecast - HIGH

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Date Sent: Wednesday, 21 August 2002 8:23 a.m.

From: Blue Skies Weather <forecasters@blueskies.co.nz>

Add to Address Book

To: "Teresa.Aberkane" <Teresa.Aberkane@ecan.govt.nz>,

Subject: Christchurch Air pollution forecast - HIGH

Status: Urgent New

AIR POLLUTION POTENTIAL FORECAST

Weather conditions forecast in Christchurch for tonight ARE LIKELY to result in high air pollution
Please use alternatives to solid fuel burning.

This advice is issued by Blue Skies Weather and Environment Canterbury.

For further information on weather conditions contact Tony Trewinnard, Blue Skies Weather, 03 3264234 or 021 2247767.
For further information on pollution levels contact Teresa Aberkane, Environment Canterbury, 03 3653828.

-- Tony Trewinnard
Blue Skies Weather & Climate Services Ltd
P.O. Box 17621
Christchurch, New Zealand
ph 03 3264234
fax 03 3264235

Secure mode active.

Appendix E PM$_{10}$ Concentration during winter 2002

Date	PM$_{10}$ ugm^{-3}	Date	PM$_{10}$ ugm^{-3}	Date	PM$_{10}$ ugm^{-3}	Date	PM$_{10}$ ugm^{-3}	Date	PM$_{10}$ ugm^{-3}	Date	PM$_{10}$ ugm^{-3}	Date	PM$_{10}$ ugm^{-3}
1/1/02	0	2/1/02	0	3/1/02	0	4/1/02	10	5/1/02	10	6/1/02	8	7/1/02	7
8/1/02	16	9/1/02	16	10/1/02	7	11/1/02	5	12/1/02	6	13/1/02	7	14/1/02	8
15/1/02	8	16/1/02	10	17/1/02	10	18/1/02	8	19/1/02	6	20/1/02	9	21/1/02	12
22/1/02	15	23/1/02	15	24/1/02	14	25/1/02	15	26/1/02	16	27/1/02	16	28/1/02	8
29/1/02	18	30/1/02	18	31/1/02	20	1/2/02	22	2/2/02	20	3/2/02	21	4/2/02	16
5/2/02	9	6/2/02	15	7/2/02	14	8/2/02	12	9/2/02	19	10/2/02	25	11/2/02	15
12/2/02	5	13/2/02	0	14/2/02	7	15/2/02	7	16/2/02	10	17/2/02	9	18/2/02	13
19/2/02	9	20/2/02	17	21/2/02	18	22/2/02	14	23/2/02	11	24/2/02	13	25/2/02	15
26/2/02	16	27/2/02	12	28/2/02	17	1/3/02	12	2/3/02	11	3/3/02	8	4/3/02	20
5/3/02	24	6/3/02	13	7/3/02	19	8/3/02	17	9/3/02	12	10/3/02	7	11/3/02	7
12/3/02	15	13/3/02	15	14/3/02	11	15/3/02	14	16/3/02	9	17/3/02	11	18/3/02	15
19/3/02	14	20/3/02	17	21/3/02	11	22/3/02	15	23/3/02	15	24/3/02	16	25/3/02	17
26/3/02	11	27/3/02	16	28/3/02	26	29/3/02	18	30/3/02	9	31/3/02	9	1/4/02	9
2/4/02	10	3/4/02	14	4/4/02	21	5/4/02	18	6/4/02	13	7/4/02	24	8/4/02	12
9/4/02	22	10/4/02	13	11/4/02	12	12/4/02	11	13/4/02	10	14/4/02	15	15/4/02	29
16/4/02	13	17/4/02	20	18/4/02	21	19/4/02	8	20/4/02	19	21/4/02	20	22/4/02	15
23/4/02	22	24/4/02	16	25/4/02	9	26/4/02	13	27/4/02	7	28/4/02	6	29/4/02	15
30/4/02	27	1/5/02	31	2/5/02	33	3/5/02	17	4/5/02	20	5/5/02	16	6/5/02	13
7/5/02	13	8/5/02	22	9/5/02	34	10/5/02	48	11/5/02	22	12/5/02	37	13/5/02	11
14/5/02	23	15/5/02	71	16/5/02	40	17/5/02	11	18/5/02	8	19/5/02	21	20/5/02	25
21/5/02	26	22/5/02	93	23/5/02	7	24/5/02	29	25/5/02	11	26/5/02	21	27/5/02	23
28/5/02	21	29/5/02	42	30/5/02	52	31/5/02	44	1/6/02	73	2/6/02	51	3/6/02	34
4/6/02	103	5/6/02	20	6/6/02	30	7/6/02	48	8/6/02	19	9/6/02	34	10/6/02	61
11/6/02	30	12/6/02	15	13/6/02	14	14/6/02	26	15/6/02	17	16/6/02	23	17/6/02	9
18/6/02	19	19/6/02	53	20/6/02	18	21/6/02	17	22/6/02	37	23/6/02	29	24/6/02	42
25/6/02	82	26/6/02	39	27/6/02	20	28/6/02	28	29/6/02	5	30/6/02	4	1/7/02	11
2/7/02	101	3/7/02	156	4/7/02	42	5/7/02	17	6/7/02	53	7/7/02	40	8/7/02	68
9/7/02	68	10/7/02	15	11/7/02	15	12/7/02	12	13/7/02	5	14/7/02	7	15/7/02	16
16/7/02	21	17/7/02	58	18/7/02	31	19/7/02	210	20/7/02	38	21/7/02	7	22/7/02	14
23/7/02	9	24/7/02	22	25/7/02	15	26/7/02	33	27/7/02	36	28/7/02	37	29/7/02	26
30/7/02	35	31/7/02	39	1/8/02	20	2/8/02	16	3/8/02	24	4/8/02	16	5/8/02	9
6/8/02	7	7/8/02	8	8/8/02	16	9/8/02	18	10/8/02	103	11/8/02	14	12/8/02	9
13/8/02	27	14/8/02	20	15/8/02	6	16/8/02	9	17/8/02	8	18/8/02	11	19/8/02	43
20/8/02	4	21/8/02	49	22/8/02	28	23/8/02	18	24/8/02	13	25/8/02	9	26/8/02	14
27/8/02	17	28/8/02	20	29/8/02	33	30/8/02	15	31/8/02	13	1/9/02	44	2/9/02	18
3/9/02	14	4/9/02	15	5/9/02	22	6/9/02	15	7/9/02	15	8/9/02	14	9/9/02	9
10/9/02	13	11/9/02	12	12/9/02	21	13/9/02	15	14/9/02	22	15/9/02	20	16/9/02	20
17/9/02	13	18/9/02	10	19/9/02	16	20/9/02	12	21/9/02	16	22/9/02	20	23/9/02	9
24/9/02	12	25/9/02	14	26/9/02	10	27/9/02	14	28/9/02	14	29/9/02	11	30/9/02	19
1/10/02	16	2/10/02	12	3/10/02	12	4/10/02	21	5/10/02	18	6/10/02	23	7/10/02	13
8/10/02	13	9/10/02	21	10/10/02	20	11/10/02	6	12/10/02	9	13/10/02	11	14/10/02	25
15/10/02	13	16/10/02	18	17/10/02	14	18/10/02	12	19/10/02	9	20/10/02	11	21/10/02	9
22/10/02	13	23/10/02	13	24/10/02	24	25/10/02	14	26/10/02	13	27/10/02	9	28/10/02	9
29/10/02	10	30/10/02	10	31/10/02	13	1/11/02	15	2/11/02	14	3/11/02	13	4/11/02	11
5/11/02	17	6/11/02	12	7/11/02	11	8/11/02	13	9/11/02	12	10/11/02	13	11/11/02	10
12/11/02	16	13/11/02	18	14/11/02	17	15/11/02	15	16/11/02	7	17/11/02	8	18/11/02	13
19/11/02	9	20/11/02	6	21/11/02	11	22/11/02	15	23/11/02	15	24/11/02	16	25/11/02	11

(shaded) >24 hour average PM$_{10}$ health guideline of 50 $\mu g/m^3$